

ADVANCED MASS SPECTROMETRIC METHODS
OF JET FUEL ANALYSIS

BY

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To the Glory of GOD
whose grace through Jesus Christ
has brought me here and is taking me there.

To O. Dean Martin
Minister of Trinity United Method Church of Gainesville
whose teachings and courage has been an inspiration in my life.

To the "Original Little Leaguer"
Harold "Major" Gehron
who passed away on November 15, 1987.

To Mom and Dad

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Abstract of Dissertation Presented to the Graduate School
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Hydrocarbon type analysis (HTA) is widely used to evaluate the chemical composition of petroleum and shale-derived products, such as jet fuels. The HTA methods provide a knowledge of the macro-composition of the jet fuels which is important in engine design and performance. Presently the methods used for HTA of jet fuels are limited by the boiling point range of the analysis and the instrumentation requirements. The HTA method for gasolines (used for jet fuels), American Society of Testing and Materials standard test method D-2789, was developed in the mid-1950s on magnetic sector mass spectrometers which are no longer commercially available.

A gas chromatography/mass spectrometry (GC/MS) method has been developed for the hydrocarbon type analysis (HTA) of jet fuels. The method employs a short-column capillary (3 meters) which is interfaced directly into a Finnigan TSQ45 tandem mass spectrometer. Advantages

of this method include employment of present day GC/MS instrumentation and simple GC sample introduction. Additionally, a simulated distillation profile may be obtained based on specific hydrocarbon types which allows for the determination of more accurate average carbon numbers of each hydrocarbon type. The results of the HTA on a series of fuels and synthetic fuel mixtures will be reported along with a complete characterization of the GC/MS/HTA method and results. The results and methodology of the GC/MS simulated distillation method for average carbon numbers will be reported.

A preliminary investigation of alternative MS techniques for jet fuel analysis has been performed for the development of methods for total fuel analysis (TFA) (determination of 95% of all components present at 0.05% weight or greater). These techniques include alternative ionization techniques such as low energy electron ionization and methane chemical ionization; and tandem mass spectrometry techniques such as daughter scan MS and parent scan MS. The application and results of these techniques will be presented in regards to the HTA and TFA of jet fuels.

CHAPTER I

INTRODUCTION

The need to understand the chemical composition of aviation fuels has never been more important than in the last decade. This need stems from two important aspects: the recent world-wide shortages of petroleum crude reserves which have resulted in a transition to alternative crude sources; and the desire to design and operate high performance jet engines with the knowledge of fuel composition as a controlling criterion. This has led to a resurgence in the development of new analytical techniques for petroleum analyses and more specifically aviation fuel analyses. In this laboratory investigations are presently underway for the application of gas chromatography/mass spectrometry (GC/MS) and GC/MS/MS for analysis of aviation fuels (in particular turbine jet fuels). There are two modes of analysis of interest, hydrocarbon type analysis (HTA) and total fuel analysis (TFA). The concept of each application will be discussed below.

Objectives

This research project is organized around two goals. The first is to develop, implement, and characterize a gas chromatography/mass spectrometry (GC/MS) hydrocarbon type analysis (HTA) for jet fuels.

These fuels represent a specific boiling point fraction or range of components of crude oil. The second goal is to begin preliminary investigations into the development of a GC/MS method for total fuel analysis (TFA) (determination of 95% of all components present at 0.05% weight or more) of these jet fuels. Vast differences in chromatographic separation will be required in these two tasks. The ability to integrate the two methods with one instrumental configuration (GC/MS) is a goal of significant importance.

Background

This section will discuss the idea of type analysis or more specifically hydrocarbon type analysis of fossil fuels and the need and significance of new methods. Total fuel analysis will also be discussed illustrating the need for specific detection systems.

Type Analysis

The concept of "Type Analysis" is not widely known among analytical chemists. One may ask, "what type (of) analysis did you perform on the samples?" And one may reply, "a type analysis was performed on the samples." Thus the confusion begins. Type analysis in general does not provide information on specific individual components in a mixture but rather supplies information on the relative amounts of certain classes of compounds. In many applications the quantitation of specific compounds is not required and may provide much more information than is actually desired. This is particularly true in cases where the analyst is only interested in the overall macro-composition of a very complex mixture. The type analysis of

hydrocarbon mixtures, such as gasoline and heavier oils, represents such an application of type analysis. Hydrocarbon type analysis is a widely used procedure for the evaluation of petroleum feedstocks and other complex mixtures. In 1951 Ralph Brown of the Atlantic Richfield Corporation developed the first mass spectrometric technique for Hydrocarbon Type Analysis (HTA) (1). The Brown method operates on the premise that certain classes of compounds or homologous series, for example paraffins, form a specific series of fragmentation ions in the electron ionization source of the mass spectrometer. In this example the paraffins form the series of mass fragments 43, 57, 71, 85, and 91. Not all species of this series form all or only these ions. Similarly the paraffin series is not the only class or homologous series of compounds which contain any of these ions. Therefore an extensive calibration scheme is required to normalize for this mixing of fragmentation series between hydrocarbon types. Details of the present method will be discussed in Chapter II, Clarification of ASTM D-2789. Since the Brown method, there have been numerous improvements on his method due to improved calibration schemes (2,3), and improved instrumentation (4,5). In 1962 standard Hydrocarbon Type Analysis methods for gasoline (6) and diesel fuels (7) were adopted into the American Society of Testing and Materials (ASTM) standards. There have been several revisions of these methods over the years, but the basis of the methods remains the same. The methods, ASTM D-2789 and D-2425, perform the analysis on magnetic sector instruments which are no longer in commercial production. Because of this limitation, there is a much greater demand for samples to be analyzed than there are laboratories

equipped to perform them. Additionally, the means of sample introduction into the mass spectrometer, which is via a heated glass inlet volume or microburette, is a time-consuming procedure and facilitates component discrimination (8). The technique also relies on manual measurements of peak height intensity which eliminates the ability to computerize the calculations. Consideration of these limitations illustrates the need for a modern HTA method performed on a widely available modern instrument.

At the 1987 meeting of The American Society of Mass Spectrometry in Denver, the ASTM committee on petroleum analyses (9) expressed interest in the development of new and/or improved methods of HTA in the fuels area. Presently several methods are used for hydrocarbon type analysis such as the fluorescent indicator adsorption (FIA) procedure which covers the determination of saturates, non-aromatic olefins, and aromatics (10). Limitations of this method include long analysis time (3-4 hours per sample), poor precision, and lack of automation capabilities. Limitations of these methods led to the development of several liquid chromatographic methods (11), but limitations of these methods include the inability to separate and quantitate enough classes. With the development of a GC/MS/HTA several advantages would be realized. First, convenience in instrumentation, since most modern analytical laboratories are equipped with a GC/MS, many laboratories will be able to perform the analysis, and the sample load will be decreased. Second, GC introduction will provide improved sample introduction techniques which are more convenient and less prone to component discrimination. Additionally, the use of chromatography

will provide information such as distribution of components as a function of boiling point and make possible the extension of the method to total fuel analysis by increasing the chromatographic resolution.

Total Fuel Analysis

The concept of total fuel analysis (TFA) is one to which most analytical chemists may relate. The objectives are to quantitatively determine specific components or classes of components of jet fuel. One must be knowledgeable of the complexity of jet fuels to appreciate the formidable task at hand. A typical jet fuel may contain from 400 up to 4000 individual components. Davis and Giddings (12) and Martin and co-workers (13) have shown theoretically that, in order to chromatographically resolve 90% of the components in a 100 component mixture, 20,000,000 theoretical plates would be required. Considering a standard capillary GC column of 0.25 mm i.d. and 0.25 μm thickness, a column length of 5 km or 3 miles would be required for such an analysis. This theoretical calculation merely illustrates the need for more selective detection methods which could utilize normal high resolution chromatography.

History and Reviews of Hydrocarbon Type Analysis

Discussions on the history of HTA of petroleum-derived mixtures such as fuels will quickly lead one to a general discussion of the early history and development of mass spectrometry. The impetus for early mass spectrometry research was generally fueled by the petroleum industry and the war-time demands on the industry to supply aviation fuels of superior quality with good quality control and assurance.

Recently there have been several review articles which deal specifically with this history (14,15). The Consolidated Engineering Corporation (CEC) enjoyed the first commercially successful mass spectrometer (CEC Model 21-101) which became the prototype instrument which was be utilized by Ralph Brown (1) in the first mass spectrometric HTA of gasoline mentioned above.

There have been many methods developed in the past for the determination of hydrocarbon types in gasolines and fuels. Some of these methods relied on rather laborious and time-consuming separations, chemical reactions, and physical determinations. One procedure developed by Kurtz et al. (16) required 24 man-hours for fractionation, chemical treatment and determination by refractive indices. Rampton (17) employed distillation, silica gel percolation, hydrogenation, and measurements of refractive indices for the determination of paraffins, cycloparaffins, aromatics, olefins, and cycloolefins. The first applications of mass spectrometry to hydrocarbon fractions were to the analysis of gaseous mixtures (18). Later, with the advent of improved mass spectrometers and inlet systems, the analysis of the lower-boiling fraction of gasolines was performed (19-21). In 1951 Ralph Brown introduced the HTA method for gasolines which represented a new concept and application of mass spectrometry. The application of MS HTA soon expanded to the analysis of heavier fractions such as kerosene and heating oils (2,22). At this time O'Neal and Wier (4) and Brown et al. (23) independently described an improved all-glass heated inlet system which would not only expand the boiling point range of MS analysis even greater, allowing for the

analysis of waxes and other low vapor pressure compounds, but also improve the precision and accuracy of the method as a whole. Of particular interest at that time was more in-depth analysis of the aromatic fractions of these complex heavier mixtures (24-27). Previous to these MS techniques, little was known of the chemical make-up of such aromatic fractions. From the middle 1950s, which may be regarded as the end of the rapid growth period of mass spectrometry research in the applications of petroleum-derived mixtures, there have been very few publications appearing in the literature. However, with the advent of high resolution mass spectrometers in the early 1960s, there was an additional surge of interest in MS techniques for the analysis of petroleum-derived complex mixtures (28-31). Traditionally, the major use of high resolution MS was for the identification and structural determination of pure compounds or major components of a simple mixture. Since heavier petroleum fractions contain such a large variety of compounds compared to lower boiling fractions such as gasoline, a single low resolution mass spectrum cannot be interpreted in terms of hydrocarbon types. The high resolution MS techniques could single out each hydrocarbon type based on the exact mass of the fragment ions and/or molecular ions. The classification scheme became known as the "Z number" classification based on the formula C_nH_{2n+z} where z is a number which represents the degree of unsaturation and/or ring closure and signifies the hydrocarbon type. A more extensive discussion on "Z number" classification may be found in the paper by Teeter (29) which introduces an improved high resolution MS hydrocarbon type analysis for 22 hydrocarbon types. This method determines the

relative amounts of eight types of saturates, ten types of aromatics, and four types of sulfur-containing aromatics. In addition to high resolution techniques a number of low resolution techniques began to appear in the literature. The Robinson and Cook method (32) followed by the Amoco method (26) took advantage of the appearance of saturate fragments at lower masses and aromatic fragments at higher masses. This enabled the spectra to be subdivided into a saturate and aromatic region allowing mathematical treatment and normalization. The elemental analysis, carbon number distribution, average molecular weight, and the general aromaticity of coal-derived distillates were determined by the combination of low-voltage, high resolution MS (33).

Other analytical techniques apart from MS techniques have been utilized in the pursuit of a suitable HTA of fuels and other complex petroleum mixtures. Based on the classic silica gel separation of saturates, olefins, and aromatics, new high performance liquid chromatographic methods have been developed which utilize silver-coated silica gel particles and n-pentane mobile phases (34). Separation of saturates, single ring aromatics, double ring aromatics, and polynuclear aromatics was obtained for olefin free kerosenes and diesel fuels using bonded aminosilane stationary phases (35). An excellent review is available on the application of HPLC and GC to hydrocarbon group analysis (36-38). Most recently several workers have evaluated supercritical fluid chromatography (SFC) for the separation of hydrocarbon types (39). Separation of paraffins, olefins, and aromatics was obtained in two reports; using SF₆ mobile phase, pressure

programming, and FID detection (40); and using silver nitrate impregnated silica gel stationary phases with CO₂ mobile phase and refractive index detection (41). Combination of SFC with MS shows great promise for future applications to fuels analysis.

Specifications of Jet Fuels

With the world-wide shortage of conventional high quality crude oils, there has been a dramatic decrease in the availability of jet fuels. As a result of this shortage, the industry has experienced a transition from petroleum sources towards utilization of alternative sources such as oil shale, tar sands, coal liquid, and heavy oils for the production of jet fuels. Additionally fuels are being synthesized by blending various refinery streams and mixing of pure compounds. This shift has created increases in processing cost as well as many uncertainties in market stability. More importantly here, new unknowns have been generated in the physical and chemical characteristics of these new source fuels. Recently it has become more important in the design and operation of jet engines to be able to correlate the physical parameters of jet fuels with their chemical composition. With the addition of these new source fuels, there is a need for new and improved physical and chemical methods of jet fuel analysis. Traditionally the determination of the physical parameters of jet fuels has been the focus of jet fuel analysis. Table 1.1 lists some of the more common physical parameters determined for jet fuels (42). The importance of a few of these parameters is as follows: thermal

Table 1.1

List of Important Physical Parameters Determined for
Aviation Fuels and the Corresponding ASTM Methods Used

Physical Parameter	Test	ASTM Method
Volatility	Distillation	D-86
	Specific Gravity	D-287
	Vapor Pressure	D-328, D-2551
Fluidity	Freezing Point	D-2386
Combustion	Heat of Combustion	D-240, D-2382
	Aniline-Gravity Product	D-611, D-287
	Knock Rating: Lean Fuel	D-2700
	Rich Fuel	D-909
Corrosion	Copper Strip Test	D-130
Stability	Potential Gum	D-873
	Precipitate	D-873
Contaminants	Existent Gum	D-381
	Water Reaction:	
	Interface Rating	D-1094
	Volume Change	D-1094
Additives	Tetraethyllead Content	D-3341, D-2599, D-2547
	Dye Content	D-2392

stability is important since jet fuels are exposed to extremely high temperatures and minimal decomposition is desired; viscosity of fuels as a function of temperature is important since the fuels must remain fluid in flights where the fuels are exposed to extremely low temperatures in storage; the density of fuels (or the volumetric energy) determines the ultimate range in miles of the aircraft. For more information on any of the specifications listed in Table 1.1, refer to the appropriate reference listed. Most methods used in the determination of the above mentioned physical parameters are ASTM standard methods and represent important contributions to fuel and jet engine research.

As mentioned above, the specifications of jet fuels are based mainly on the physical parameters or usage requirements. The single composition requirement common to all aviation fuels is they must consist almost completely of hydrocarbon compounds. There are specific limitations on particular hydrocarbon types such as aromatics and olefins due to performance criteria. Additionally, low level additives may be present as well as low level contaminants of various sorts.

Jet fuels or more specifically turbine jet fuels are made up of hundreds of hydrocarbons that may be divided into four subgroups or hydrocarbon types: paraffins and isoparaffins (branched paraffins); cycloparaffins or naphthens; aromatics; and olefins. The former two types make up the saturates and the latter two types the unsaturates. Figure 1.1 illustrates some example compounds of each hydrocarbon type.

Paraffins and cycloparaffins are generally the major type component of jet fuels. The paraffins are the most stable components and do not

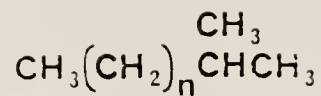
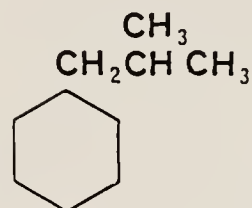
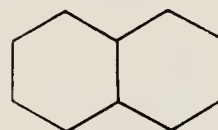
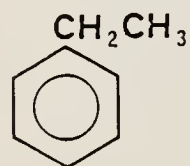
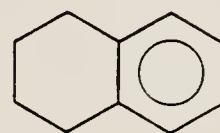
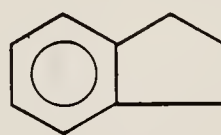
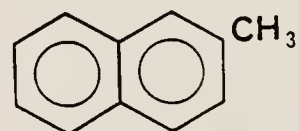
Paraffin*Monocycloparaffin**isopropyl-cyclohexane**Dicycloparaffin**decalin**Alkylbenzene**ethylbenzene**Indane/Tetralin**Naphthalene**2-methylnaphthalene*

Figure 1.1. Structures of some example compounds representative of the six hydrocarbon types. Some specific examples are also shown.

readily react with materials in which they come in contact with such as elastomers, paints, and various metals. They are clean-burning compared to other hydrocarbons and have a very high heat release per unit weight. Both of these advantages are due to the high hydrogen-to-carbon ratio. Cycloparaffins have a lower hydrogen-to-carbon ratio which lowers their heat release per unit weight, but increases their density or volumetric energy. Cycloparaffins are also clean-burning and stable and have a lower freezing point compared to paraffins of equal carbon number.

Aromatics are fully unsaturated ring structures which may also incorporate saturated structures. Because of the very low hydrogen-to-carbon ratio, they have a much greater volumetric energy but a lower heat release per unit weight than the paraffins. The aromatics are reactive and tend to cause swelling of rubber seals. They produce large amounts of smoke while burning, and a high-luminosity flame. This particular aspect is important when considering secret reconnaissance missions of the Armed Forces. Because of these factors the maximum concentration of aromatics permitted in jet fuels is 20-25% Virgin fuels generally contain no more than 10-20% aromatics.

Olefins are the most reactive hydrocarbon types and are capable of reacting with many materials. They react with air to form varnishes or rubber-like materials. They can dimerize or polymerize forming high molecular weight contaminants. Because of their high reactivity, olefins are generally not found in natural or virgin crudes. They may, however, be formed in the refinery cracking processes. Specifications

limit the content of olefins to less than 5 percent in order to reduce varnish and gum formation.

Other non-hydrocarbon types which may be found in aviation fuels include heteroatomic species such as sulfur-, oxygen-, and nitrogen-containing compounds. These include mercaptans, sulfides, thiophenes, and free sulfur as example sulfur types; alcohols and naphthenic acids as example oxygen types; and aza and amino polynuclear aromatics as example nitrogen types. Combinations of these contaminants tend to form high molecular weight gums and deposits when exposed to air during storage. This creates many problems such as filter clogging, sticking of valves, and plugging of orifices. Additives present which help to eliminate some of these problems include antioxidants, metal deactivators, fuel icing inhibitors, and corrosion inhibitors.

Instrumental Methods of Analysis

Sample Introduction

The utilization of GC/MS techniques can provide more up-to-date methods of sample introduction into the mass spectrometer. This is a direct advantage over the traditional ASTM methods, in which a heated glass inlet or microburette is employed, and the sample is introduced by effusion through a small orifice. A small fraction of the total sample is analyzed with the microburette technique, in order to minimize component discrimination which increases as the effusion of the sample into the mass spectrometer proceeds. The method is time-consuming and requires the maintenance of many instrumental parameters. The GC/MS technique will vaporize the entire sample and analyze the

entire volume which has been loaded onto the column. Because of the possibility of component discrimination during sample loading onto the GC column, component discrimination must be evaluated as a function of injection port temperature and injection techniques.

Short Column GC/MS and Simulated Distillation

An important concept of this HTA method is that chromatographic resolution of the jet fuel components is not a matter of pursuit. Trehy, Yost, and Dorsey (43) have discussed some of the important instrumental considerations of normal GC/MS using short capillary columns. In the GC/MS/HTA application of short capillary columns, the GC is mainly used as a convenient device for sample introduction into the mass spectrometer. The short columns, along with providing short analysis times, provide the ability to observe the distribution profile of the eluting jet fuel as function of column temperature. This concept is similar to that of simulated distillation (44,45) which has been utilized by the petroleum industry for many years to provide a breakdown of the boiling point distribution of the hydrocarbon mixture. The area percent of the eluting fuel is determined at various points along the profile or chromatogram. Each area percent corresponds to a specific retention time or boiling point. These boiling points are determined by a parallel eluting sample of n-paraffin homologous series in which the boiling points are known. A non-polar column must be employed to assure the correlation of retention to boiling point. The temperature corresponding to the 50 percent area point corresponds to the average boiling point of the fuel. This is a useful physical parameter, although the extraction of an average carbon number from the

results is not accurate. Application of GC/MS, however, can provide not only average boiling points but also average carbon number. This is provided by the ability of the mass spectrometer to distinguish between hydrocarbon types within the fuel mixture. Corresponding homologous series may be compared to the corresponding ion summation chromatogram of the particular hydrocarbon type and an average carbon number may be obtained. These experiments represent an important advancement in the development and understanding of hydrocarbon type analysis.

Long Column GC/MS for TFA

The quest for a GC/MS technique for TFA will require high resolution (long-column) capillary gas chromatography. Since only a select number of chromatographic peaks will be pure components, additional selectivity in addition to chromatographic resolution will be required. Many researchers have reported work in the fuels area with chromatography alone (46,47). Here the application of MS, which includes various modes of ionization, and MS/MS will be evaluated for means of chromatographic peak deconvolution. There have been numerous reports in the literature which have applied GC/MS techniques to fuel analysis. Gallegos (48) has described a high resolution GC/MS method for the analysis of a shale derived oil. Aczel has determined compound type distribution in refinery streams and synfuels using GC/MS (49). The compound distribution of a jet fuel has been determined by recombination of separately determined components using GC/MS (50).

Ancillary Jet Fuel Analysis Techniques

The development of GC/MS methods for total fuel analysis (TFA) will require the utilization of ancillary MS techniques such as low-energy electron ionization, chemical ionization, and MS/MS techniques. These techniques, when combined with chromatographic separation, will provide specific detectors for the deconvolution of multicomponent chromatographic peaks discussed earlier. The following is a review of the application of such MS techniques.

Alternative Ionization Methods

Chemical ionization (CI) (51) is a softer ionization technique which is capable of producing an increased abundance of molecular ion and minimal fragmentation compared to conventional electron ionization (EI). Harrison discusses the use of CIMS with various reagent compounds for the characterization of hydrocarbons (52). Although there have been significant applications of CI to the characterization of single classes of compounds in fuels and other complex mixtures, there have been no known publications on the application of CI to an overall hydrocarbon type analysis of jet fuels. Sieck characterized gasolines for their aromatic content using low-energy photoionization cyclohexane CI (53). Sieck, Burke, and Jennings (54) used N_2O CI for screening of aviation fuels. The OH^- ion was employed for negative ion CI, which eliminated ionization of aliphatic compounds. Other applications of CIMS have been devoted to the determination of polynuclear aromatic hydrocarbons (PAH) in fuels (55), as well as aza and amino PAH in coal derived liquids (56). Negative ion ammonia CI GC/MS has been used for the quantitation of sulfur-containing compounds

in gasoline (57). Bauer, Schubert and Enke (58) used methanol CI for the characterization of heterospecies in the presence of hydrocarbons. The essential aspect of CI GC/MS techniques in regard to total fuel analysis is the ability to deconvolute co-eluting components of the fuel. In the current research only methane chemical ionization is evaluated.

Electron ionization (EI) is considered the work-horse of mass spectrometry. One aspect of EI/MS which is rarely explored in petroleum analysis is the utilization of low-energy EI. Since various compound types have different ionization potentials, these differences may be utilized as a source of compound-type discrimination. One of the earliest applications of low-energy ionization MS (referred to as low-voltage MS) was the determination of the unsaturated hydrocarbon fraction in a petroleum naphtha (59). In this method only molecular ions of the unsaturated species are formed, thus eliminating saturate interferences. Aczel and Johnson utilized low-energy electron ionization in conjunction with high resolution MS for the analysis of aromatic fractions of complex petroleum mixtures (31). As mentioned above, low energy photochemical ionization was used for the analysis of aromatics in gasoline (53). The use of low-energy electron ionization GC/MS is evaluated here for the characterization of separate hydrocarbon classes. This technique and its usefulness will be discussed.

Mass Spectrometry/Mass Spectrometry

Mass spectrometry/mass spectrometry (MS/MS) is quite useful for the direct analysis of complex mixtures such as coal derived liquids.

Recently there have appeared in the literature many applications of MS/MS to the analysis of complex petroleum mixtures (56,58,60-71). There exist two MS/MS instrumental techniques which are generally used, mass-analyzed ion kinetic energy spectrometry (MIKES) (72,73) and triple quadrupole mass spectrometry (TQMS) (74). To date, no known application of MS/MS to HTA of fuels has appeared in the literature; however, as with CI applications, most MS/MS applications have been dedicated to the determination of a single class of compounds or a single component. In the current research, several aspects of TQMS have been evaluated for possible HTA methods or TFA methods of jet fuels. These results will be discussed along with the possibility of combining MS/MS with alternative ionization techniques.

Outline of Thesis

The remainder of the thesis is divided into five chapters. Chapter II, Experimental, will describe all experimental, instrumental, and computational techniques. Chapter III, Gas Chromatography/Mass Spectrometry/Hydrocarbon Type Analysis, will contain experimental results and discussions based solely on the development, implementation, and characterization of the GC/MS/HTA method. Chapter IV, Alternative Ionization Techniques, will contain results and discussions on the use of these techniques in the application of TFA and HTA of jet fuels. Chapter V, Gas Chromatography/Mass Spectrometry/Mass Spectrometry, will contain results and discussions on the use of GC/MS/MS in the application of TFA and HTA of jet fuels.

Finally Chapter VI, Conclusions and Future Work, will summarize the total effort and describe suggested future work. As in any research effort each question answered brings about several new questions. This project is no exception.

CHAPTER II

EXPERIMENTAL

The following chapter will discuss the experimental parameters which are involved in the development, characterization, and implementation of the hydrocarbon type analysis of jet fuels. The experimental parameters which deal specifically with studies in total fuel analysis, such as chemical ionization and MS/MS will be discussed in those specific chapters. The general experimental parameters, such as materials, jet fuel preparation, and instrumentation will also be discussed here.

Materials

All chemicals were ACS grade unless otherwise specified and were used as received without further purification. Standards were purchased from various vendors and were used as received without further purification. All jet fuel samples were obtained from Pratt & Whitney-Fuels Division, West Palm Beach, Florida. The fuels were shipped at ambient temperatures without refrigeration in vials with screw-cap or crimped cap teflon-lined replaceable septa. After every use in the laboratory, the septa were replaced with new ones and samples were refrigerated at 5 C.

Apparatus

Mass Spectrometer

A Finnigan MAT TSQ45 gas chromatograph/triple-stage quadrupole mass spectrometer/data system was used in all GC/MS studies. An electron energy of 70 eV and an electron current of 300 μ A were used. The mass spectrometer was mass calibrated with FC43 (perfluorotributylamine) in accordance with the instrument's specifications. The mass spectrometer was tuned, also with FC43, to obtain a specific ion intensity ratio of m/z 69 to m/z 219, and m/z 502 to m/z 220. These ratios were monitored to insure reproducible relative abundances of the fragmentation pattern in regards to instrumental tuning alone. The low mass ratio is of greater importance in these studies since this is the general mass range in question. The mass spectrometer was scanned from 35 to 650 amu at a total scan time of 1.0 s. The electron multiplier was operated between 950 and 1000 V, with the conversion dynodes at ± 3000 V. The preamplifier gain was set at 10^8 V/A with the fine adjustment (zeroing) set for minimal acquisition of baseline noise. The mass spectrometer was interfaced to a Finnigan Model 9610 gas chromatograph. All GC operations were under computer control. The capillary GC columns were inserted directly into the ion source of the mass spectrometer through a heated interface. The ion source pressure was 0.3-0.6 Torr depending on the column head pressure. The ion source temperature was 190 C.

Gas Chromatography Conditions

A 3 m DuraBond fused silica bonded phase open tubular (capillary) column (J&W, Rancho Nuevo, CA) with an inner diameter of 0.25 mm and a

DB5 bonded phase (SE-54 equivalent or 5% phenyl-methyl silicone) of 1.0 μm thickness was operated at a head pressure of 8 pounds per square inch of helium carrier gas. Split-type injection was used with a split flow of 50 mL/min and a septum sweep of 2 mL/min. The injection port temperature was 250 C and the transfer line was 280 C. The injection port teflon lined septum was replaced after 30 - 40 injections and the injection port glass insert was checked frequently and cleaned whenever needed. The column temperature was programmed from 50 C to 250 C at 15 C/min after a hold time of 1 minute. Usually the column would not require the full temperature to elute the entire jet fuel sample. Generally 0.5-1.0 μL injections of neat jet fuel samples were made. The injection technique used was as follows in order to reduce injection error: the GC injection syringe (Hamilton) was thoroughly rinsed between samples with hexane, followed by the sample jet fuel of interest; the sample volume was pulled up from the needle volume into the syringe volume; the needle was inserted into the GC injector; a count of three allowed the needle to come to equilibrium temperature; the sample was injected at a rate of approximately 1 $\mu\text{L/s}$; this position was held for a count of three and the needle was removed. This method decreases injection discrimination due to uneven heating of the needle and components contained therein (75,76).

Other Gas Chromatographic Studies

Besides GC/MS, studies involved the application of GC with flame ionization detection. A Varian 3300 gas chromatograph was used with a flame ionization detector (FID). The same chromatographic conditions were used as stated above including the column head pressure. However,

although the column head pressures were equivalent for the two systems, different flow rates would result due to the different exit pressures. This instrument was used for the studies of component discrimination as a function of injection port temperatures and injection modes (split, splitless, and on-column). Acquisition of peak area, peak height, and retention time was obtained with an IBM 9000 minicomputer and the IBM CAPMC4 Chromatography Applications Program. Additionally, the FID system provided two advantages: a continuous mode of detection which resulted in more highly resolved chromatograms, and increased sensitivity (compared to full scan MS) which when combined with high resolution gas chromatography (longer columns, 30 meters) would demonstrate the extreme complexity of the jet fuels.

Data Handling Techniques

This section covers aspects of the data handling and reduction which proved to be a major effort in obtaining the stated goals. Considering the hydrocarbon type analysis alone, the mathematical computations were quite abstract and had to be figured out conceptually before application could be made. Below, these computations will be discussed, along with the hardware used and the software generated to deal with them.

Clarification of ASTM D-2789

The purpose of this section is to clarify the computational aspects of ASTM D-2789 standard test method (6), which is the computational basis of the GC/MS/HTA method developed here. The ASTM method, as it is referred to, determines the volume percent of six separate

hydrocarbon types in low olefinic gasolines: paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes, indanes and tetralins, and naphthalenes. Each hydrocarbon type is determined based on a characteristic set of ions as shown in Table 2.1. The method also calculates the average aromatic and average paraffinic carbon numbers based on mass spectral data. Calculations are made based on the inverse calibration tables shown in Table 1 of the ASTM D-2789 standard method (6) and are dependent upon the average carbon numbers. It is these aspects of the ASTM method, development and application of the inverse calibration matrices, which require clarification. The calculations are similar to six simultaneous equations with six unknowns; however, the unknowns are made up of a complex array of variables and the set of equations used are chosen based on two other variables as well.

The inverse calibration matrices were prepared by determining the values $\Sigma 43/T$, $\Sigma 41/T$, etc. for each hydrocarbon class mixture at each carbon number, where $T = \Sigma(\Sigma 43 + \Sigma 41 + \Sigma 67 + \Sigma 77 + \Sigma 103 + \Sigma 128)$, the sum of all the characteristic hydrocarbon sums (Σ). The compositions of the hydrocarbon class mixtures at each carbon number (up to carbon number nine) used in these determinations are given in Table 3 of the ASTM standard (6). Consider this example calculation of the inverse calibration matrix for carbon number six: the $\Sigma 43/T$, $\Sigma 41/T$, $\Sigma 67/T$, and $\Sigma 77/T$ are determined for each of the three hydrocarbon type mixtures as shown in the ASTM Table 3 under C6 blends. The results are given in Table 4 of the ASTM standard (6) under the appropriate hydrocarbon type and C6 listing along with the results for larger carbon numbers. For a

Table 2.1

The Characteristic Ion Summations Used For Each Hydrocarbon Type
in the Hydrocarbon Type Analysis

<u>HYDROCARBON TYPE</u>	<u>MASSES OF EACH CHARACTERISTIC ION SUM (Σ) (m/z)</u>
PARAFFINS	$\Sigma 43 = 43+57+71+85+99$
MONOCYCLOPARAFFINS	$\Sigma 41 = 41+55+69+83+97$
DICYCLOPARAFFINS	$\Sigma 67 = 67+68+81+82+95+96$
ALKYLBENZENES	$\Sigma 77 = 77+78+79+91+92+105+106+119+120+133+134$ $147+148+161+162$
INDANES/TETRALINS	$\Sigma 103 = 103+104+117+118+131+132+145+146+159+160$
NAPHTHALENES	$\Sigma 128 = 128+141+142+155$

given hydrocarbon type, all values (Σ/T) are divided by the largest value of that set. The numbers are arranged in a matrix in proper order. All elements of the array are then multiplied by an appropriate pressure sensitivity factor. Table 5 of the ASTM standard (6) gives the pressure sensitivity factors for each hydrocarbon class and carbon number. These values represent the instrumental response as a function of microburette pressure. The means of measuring the amount of sample introduced into the mass spectrometer was via this monitoring procedure. The C6 matrix is then inverted after multiplication by the pressure sensitivity factors. The methods used for inverting a 3x3 and 3x4 matrix (77) are shown in Appendix A; this procedure is best handled by computer programs. The elements of the C6 matrix are then multiplied by the corresponding liquid volume factors, also given in Table 5 of the ASTM standard, which are an indication of the liquid volume per unit pressure. The matrix values are then divided by 100 and are in units of volume/counts.

Examination of the elements of the inverse calibration matrices reveals much information on the use of the table. The carbon number 6 matrix illustrates this quite well. A relatively large positive entry, such as +0.009016 for $\Sigma 43/T/\text{paraffins}$, is a good similarity coefficient, as expected since paraffins response will contain a large abundance of $\Sigma 43$ ions. Similarly, the -0.000003 for $\Sigma 77/T/\text{paraffins}$ indicates a low similarity coefficient, which is also expected since very little $\Sigma 77$ ions will be present for paraffin compounds. The inverse relationship of these numbers represent the normalization function of the inverse calibration matrices described above. A

thorough evaluation of the application of the inverse calibration matrices will not be made since the method is quite common in multicomponent analysis problems. The method involves the multiplication of a 1x6 matrix (a paraffinic 1x3 and a aromatic 1x3) to a 6x6 matrix and normalizing the results to 100%. However, as mentioned above, the matrix used is dependent upon the average carbon number of the sample in question. Since an integral average carbon number is rarely obtained, two inverses should be applied with weighted results. An example calculation of the GC/MS/HTA method is given in Appendix B.

Computer Hardware and Software

The GC/MS/HTA method required extensive computations once the mass spectral data had been obtained. This is evident from the discussion above which described the methods and complexities of the calculations used. A series of TURBO BASIC programs was written to completely automate these computations. Additionally, a terminal emulator program (Persoft, Smarterterm 240) was utilized for the direct transfer of data from the MS data system to an IBM PC. The program used for calculating the volume % results and the average carbon numbers is shown in Appendix C. Other programs included an inverse calibration development program for carbon number 6; and a program which translates the emulator-captured data to usable format for the HTA program.

Ion Summation Chromatograms

The characteristic ion sums listed in Table 2.1 were plotted as separate mass chromatograms. These mass chromatograms, as shown in Figure 2.1, are referred to as ion summation chromatograms and

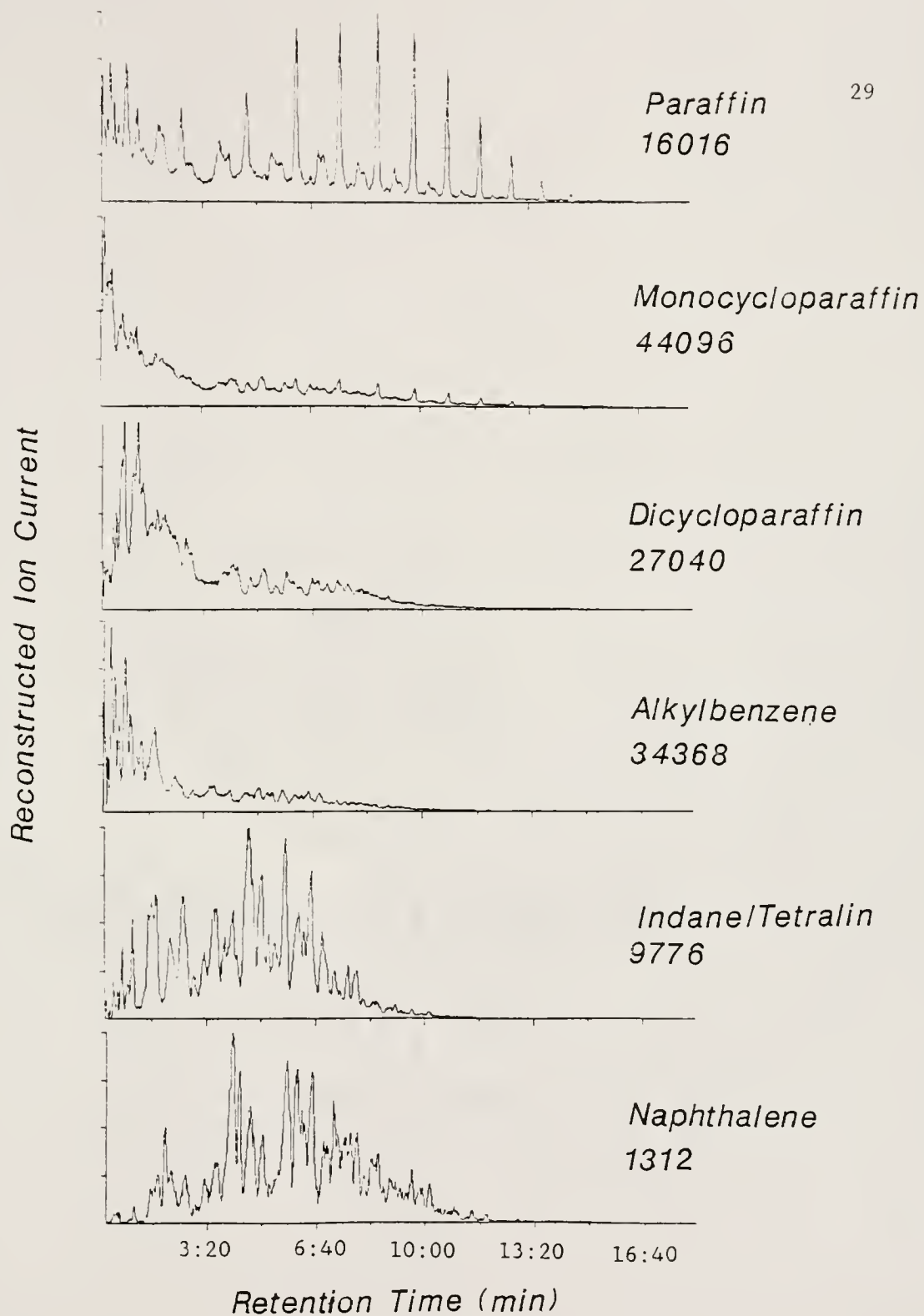


Figure 2.1. The ion summation chromatograms of each hydrocarbon type with the relative areas of each for jet fuel JP-8X 2414.

represent the chromatogram of each ion sum listed in Table 2.1. The area of each ion summation chromatogram was determined and normalized to 100%. The area percents were then calibrated with the ASTM inverse calibration matrices after determination of the average aromatic and average paraffinic carbon numbers. All these calculations were done automatically, as mentioned above.

Simulated Distillation for Determining Carbon Numbers

The application of ion summation chromatograms provided the opportunity to investigate the average carbon numbers of the jet fuels. Figure 2.2 illustrates how the average aromatic carbon number was obtained using this method. The ion summation chromatogram represents the aromatic ion series. After determination of the area centroid of this chromatogram the line may be projected down to the chromatogram of the corresponding homologous series. The value indicates the aromatic average carbon number of the fuel. Variations were made using this technique, such as combinations of ion summation chromatograms, as will be discussed in the next chapter.

Occupational Hazards

As a final note, the occupational hazards of working with jet fuels are quite evident considering the nature of these complex mixtures. It should go without saying to avoid exposure to these materials by using a well ventilated hood, wearing gloves, and keeping the samples in properly sealed vials. The major concern of working with these fuels is the effect of long term exposure. Many of the components in these mixtures are fat-soluble and therefore bio-accumulation is likely (78).

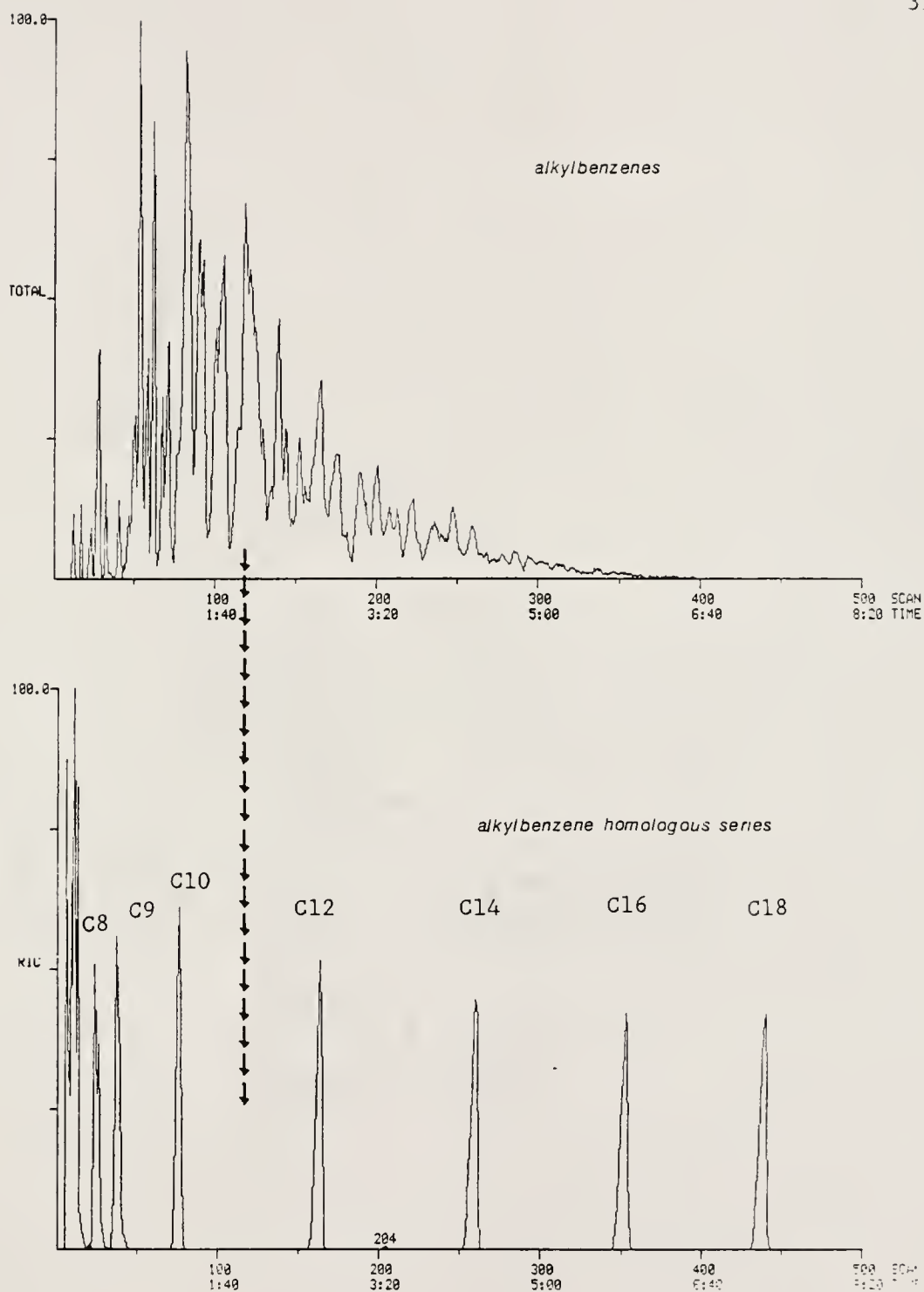


Figure 2.2. The aromatic ion summation chromatogram of a jet fuel JP-8X 2414 on a 3 meter DB5 column. The centroid of the total area, indicated by the arrows, is referenced to the alkylbenzene homologous series. The carbon number is calculated to be 10.95.

CHAPTER III

GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC
HYDROCARBON TYPE ANALYSIS

Characterization of the hydrocarbon type analysis (HTA) method was performed by evaluation of simple and complex synthetic mixtures, perturbation of jet fuels, and comparison of results to existing ASTM results. The experiments performed were to determine the effects of various instrumental and method parameters on the results of the HTA of jet fuels. The results of these experiments, as well as the simulated distillation method for the determination of average carbon numbers, will be discussed.

GC Sample Introduction

With the application of gas chromatography (GC), a new method of sample introduction into the mass spectrometer was used for HTA. It was therefore important to evaluate the specifics of sample discrimination with respect to this sample introduction technique. There are several injection techniques used in capillary gas chromatography. These are split and splitless, which depend on the flash vaporization of the sample within a heated glass-lined injection volume, and on-column injection which allows the sample to be loaded directly onto the capillary column at ambient temperatures. Specifics

of these capillary GC injection techniques are discussed elsewhere (75,76). An aromatic mixture containing C12, C14, C16, and C18 straight chain alkylbenzene in equal concentrations was used for the evaluation of component discrimination. The effect of injection port temperature and injection technique was evaluated. Figure 3.1 and Figure 3.2 illustrate the effect of injection port temperature on component discrimination for splitless and split injections, respectively, with flame ionization detection. In both cases the ratios of peak areas were normalized to the C14/C12 ratio at the 280 C injection port temperature to help illustrate the matter of discrimination. Both cases indicate component discrimination taking place at lower temperatures by the ratios being lower. This was due to less efficient vaporization of the heavier components at lower temperatures, as was expected. As the temperature was raised, the ratios increased and leveled off, indicating a lack of discrimination and the absence of component decomposition at higher injection port temperatures. A larger degree of discrimination takes place for the higher carbon number alkylbenzenes, as indicated by the larger ratio spread between the low and high injection port temperatures. The splitless technique more clearly illustrates these trends. A minimum injection port temperature of 250 C should therefore be maintained to avoid component discrimination. These results also demonstrate the improvement in reproducibility obtained using splitless injections over that obtained with split injection technique. A similar evaluation of component discrimination was performed on the GC/MS instrument. Figure 3.3 illustrates the results which are similar to those from the GC/FID

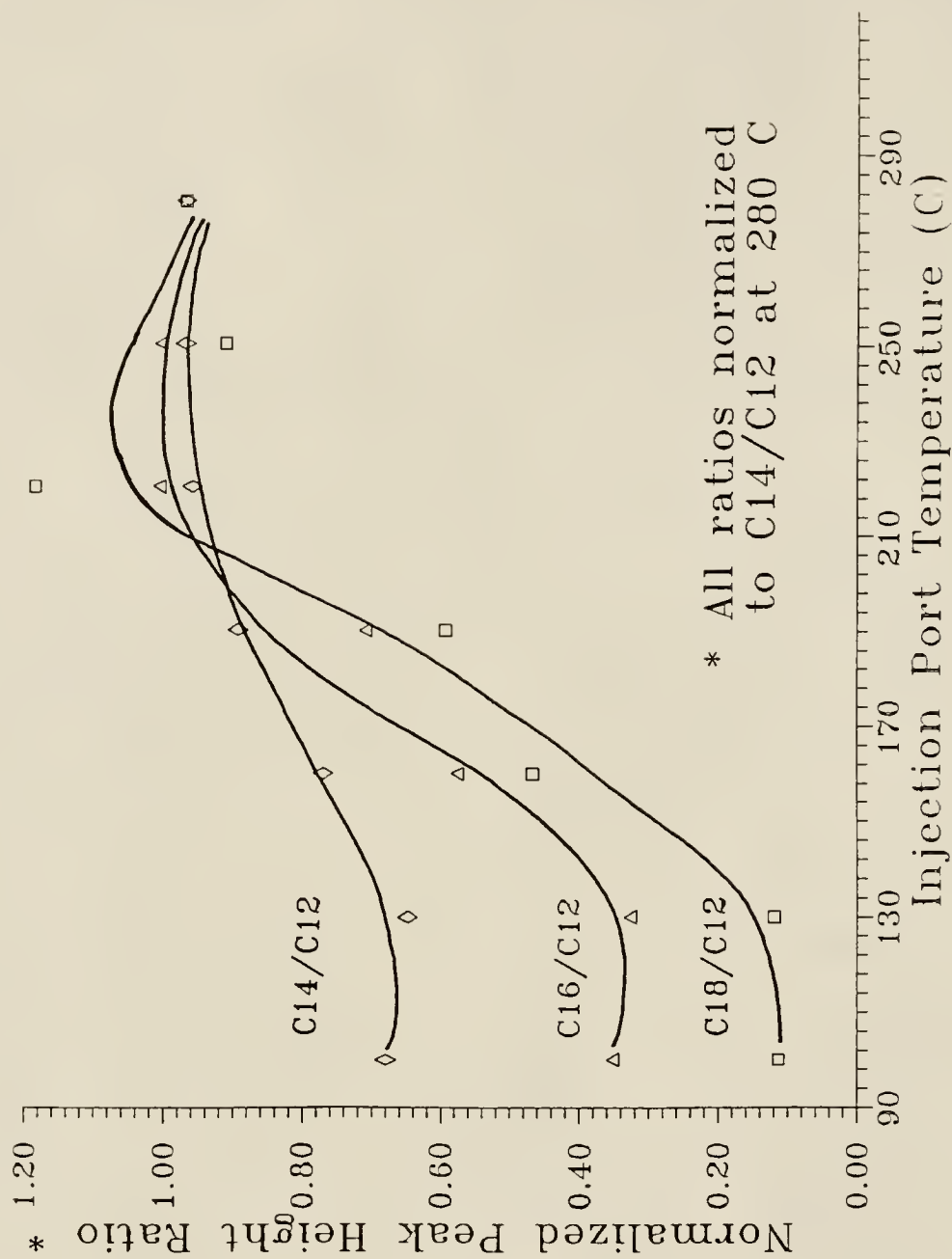


Figure 3.1. Plot of injection port temperature versus area ratios of C12, C14, C16, and C18 alkylbenzenes for splitless injections on a 3 meter DB5 capillary column, with FID detection.

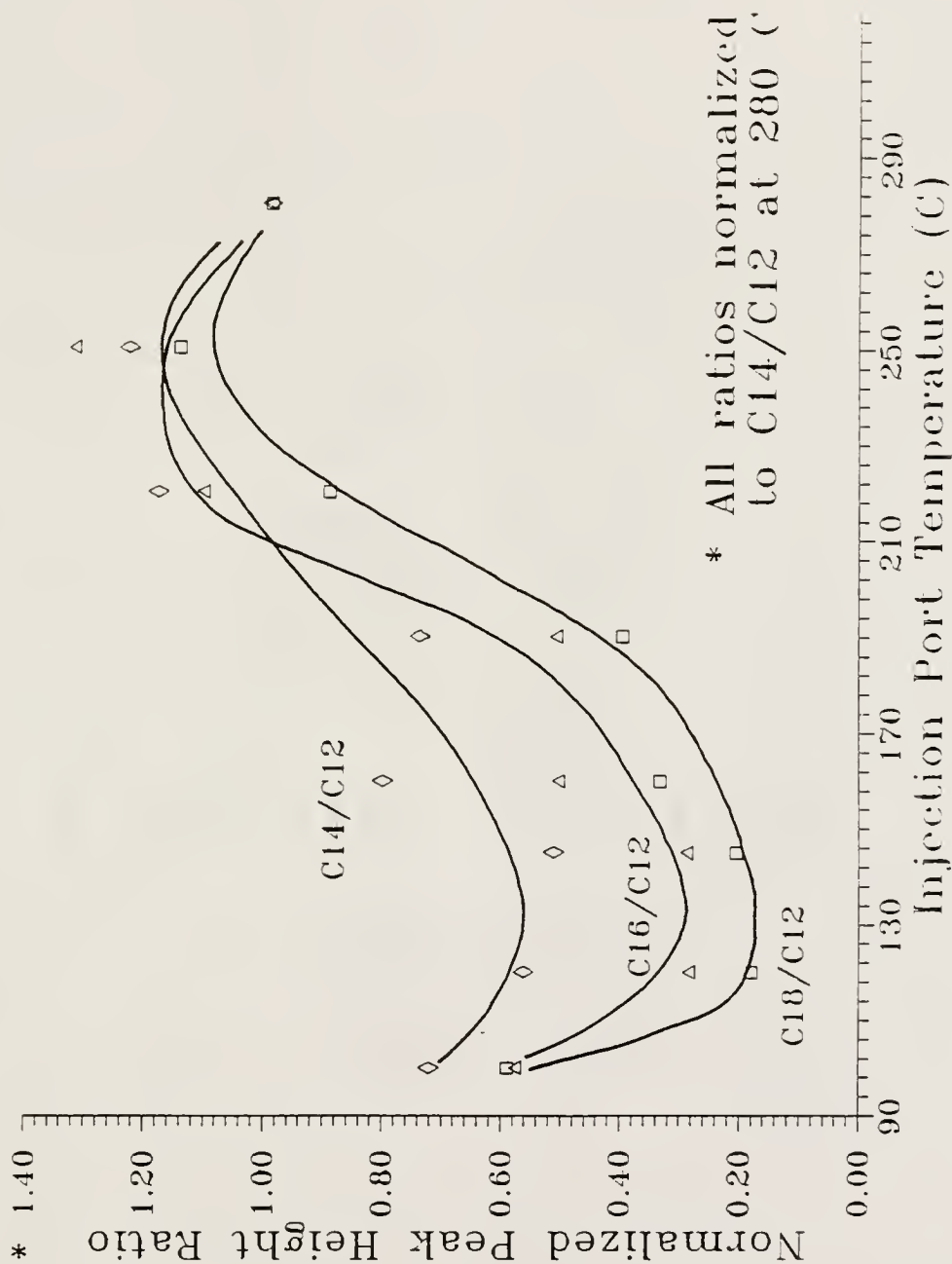


Figure 3.2. Plot of injection port temperature versus area ratios of C12, C14, C16, and C18 alkylbenzenes for split injections on a 3 meter DB5 capillary column, with FID detection.

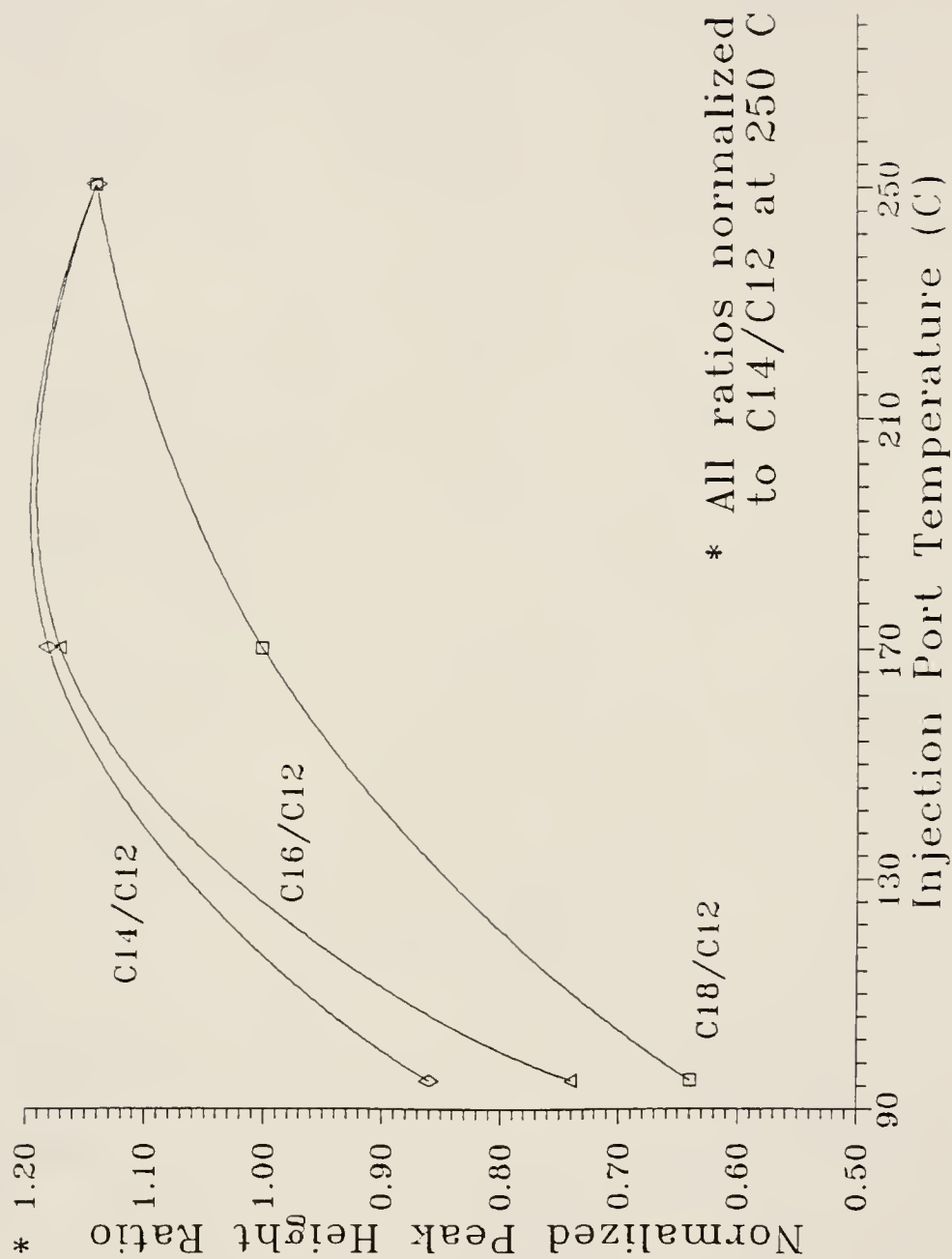


Figure 3.3. Plot of injection port temperature versus area ratios of C12, C14, C16, and C18 alkylbenzenes for split injections on a 3 meter DB5 capillary column and MS detection.

technique. However, discrimination effects are less with GC/MS, as indicated by the smaller spread of area ratios compared to GC/FID. The vacuum outlet conditions result in a large pressure drop across the short capillary column, giving higher flow rates and decreased discrimination as a function of injection port temperatures.

On-column injection was also evaluated in terms of component discrimination. It has already been demonstrated that on-column techniques provide the best precision when compared to the other modes of injection (79). Figure 3.4 illustrates component discrimination as a function of initial column temperature. The initial column temperature in on-column injection corresponds roughly to the injection port temperature in split/splitless injections. For this reason, evaluations were not possible at initial column temperatures above 120 C, since the early eluting C12 alkylbenzene component was lost in the solvent front. The results indicated no discrimination, as would be expected for on-column injections. However, there appears to be a small enhancement effect for the less volatile components at lower initial column temperatures. This cannot be explained at the present time. Table 3.1 compares splitless and on-column injection techniques for accuracy and precision. A mixture containing known weight ratios was prepared and analyzed with GC/FID. The FID response is proportional to the mass flux of analyte, and therefore direct correlations may be made between weight ratios and area ratios. Results for both splitless and on-column injections were high compared to the actual weight ratio, which may be due to some systematic error.

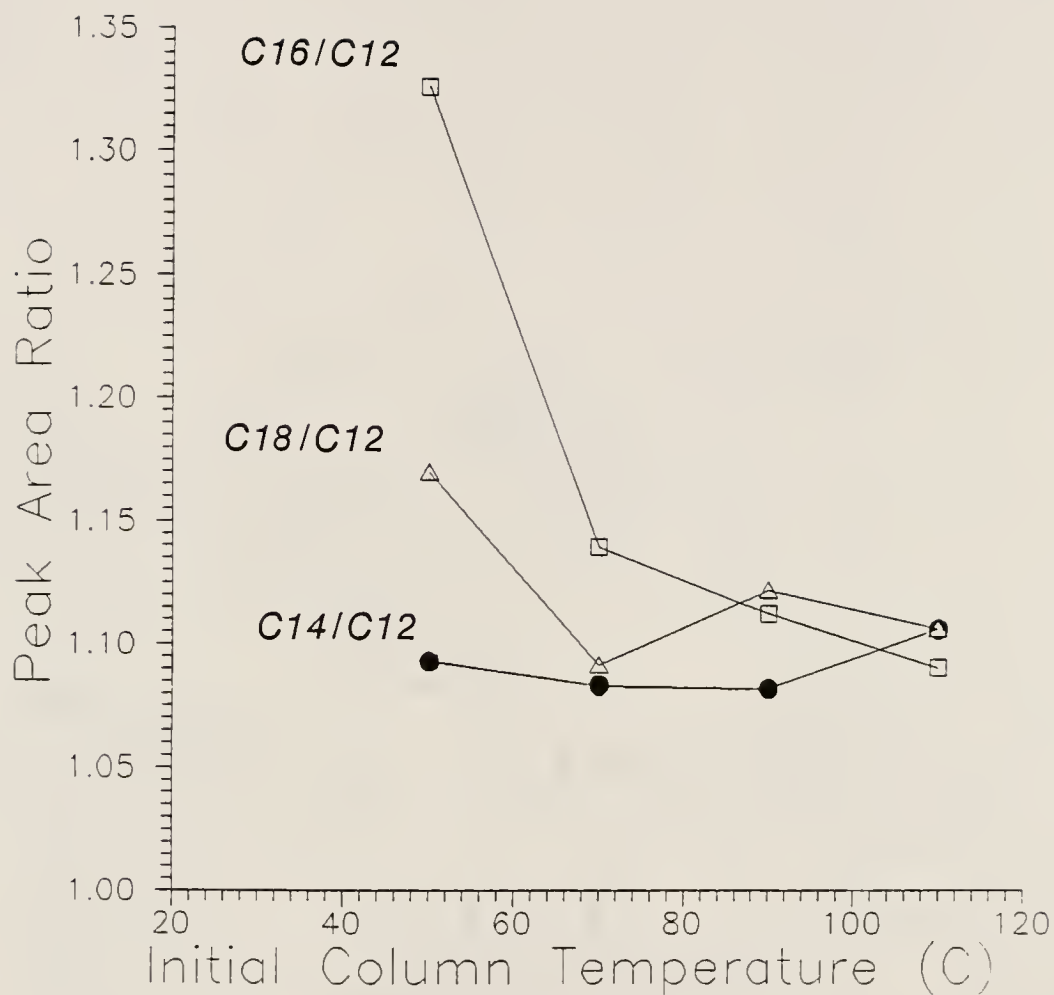


Figure 3.4. Plot of initial column temperature versus area ratios for C12, C14, C16, and C18 alkylbenzenes for on-column injections on a 3 meter DB5 column with FID detection.

Table 3.1

Comparisons of Accuracy and Precision of Area Ratios of Various Components Between Splitless and On-Column Injection Techniques

	<u>Butylbenzene</u> Decane	<u>Hexamethylbenzene</u> Decane	<u>t-Stilbene</u> Decane
Actual Wt. Ratio	0.785	0.280	0.374
Splitless			
Area Ratio	0.894(.005)	0.30(.01)	0.41(.03)
%RSD	0.54	4.32	7.24
On-Column			
Area Ratio	0.905(.004)	0.330(.009)	0.49(.01)
%RSD	0.44	2.82	2.02

Note:

number of replicates n=3

number in parenthesis indicates standard deviation

The splitless results agreed more closely with the weight ratios, while the precision of the on-column results was somewhat better.

These results indicate that, as long as the minimum injection port temperature is maintained, component discrimination is greatly reduced if not eliminated. Also, better reproducibility is obtained using splitless injections.

Ancillary Short-Column Experiments

The use of short (3 m) capillary columns in these studies has led to the discovery of some interesting chromatographic aspects. The injection technique previously described in the Experimental chapter, in which the bulk of the sample volume was removed from the syringe needle volume in order to let the needle equilibrate to the injection port temperature, was used to eliminate component discrimination and to obtain more reproducible injections. This technique when used with short columns, however, leads to the splitting of the early eluting chromatographic peaks (Figure 3.5). This was determined to be a function of injection port temperature. At high injection port temperatures, the residual amount of sample which remains in the syringe needle is vaporized prior to the injection and vaporization of the sample contained in the syringe itself. This results in a "pre-peak" at high injection port temperatures which is absent at the lower injection port temperature.

It was also observed that splitless injections provide better chromatographic resolution than on-column techniques for short capillary columns. This is presumably due to the large amount of band

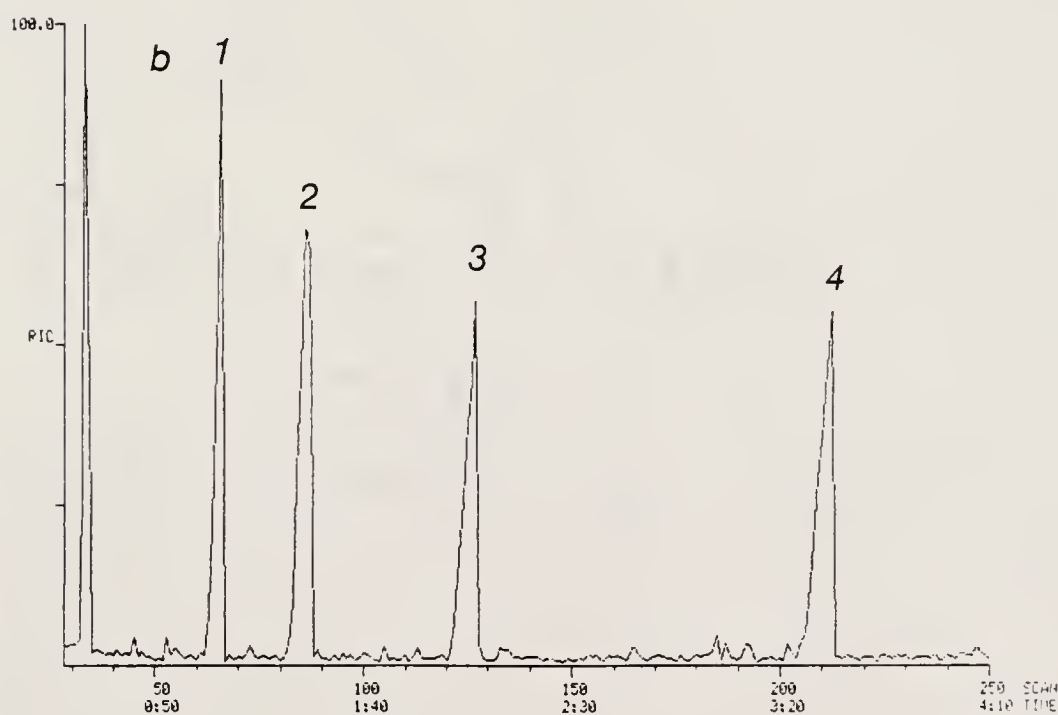
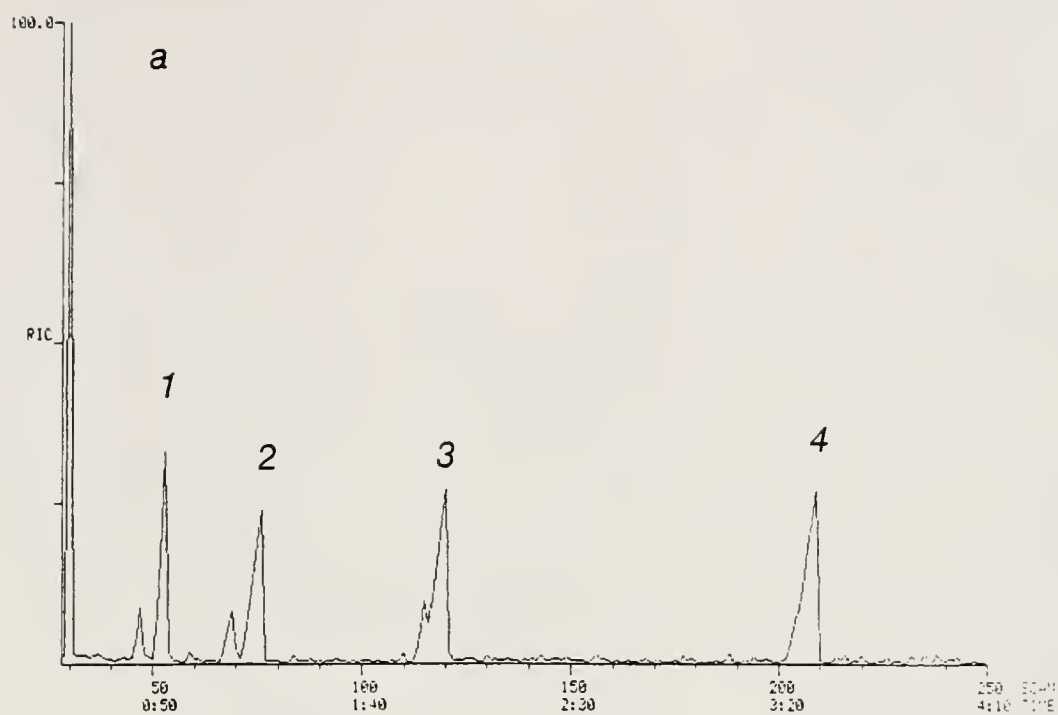


Figure 3.5. Chromatograms of nonane (1), cyclooctane (2), propylbenzene (3), and decalin (4) using split injections on a 3 meter column, a) injection port 280 C, b) injection port temperature 130 C.

spreading incurred for on-column injections relative to the column length. Figure 3.6 and Figure 3.7 illustrate the comparison of injection techniques for chromatographic resolution for a narrow boiling point range fuel and a wide boiling point range fuel, respectively. The improved chromatographic resolution for the splitless case is indicated by the sharper peaks, which are most noticeable for the late eluting peaks.

Analytical Figures of Merit

The limits of detection which are determined here do not reflect the limits that would actually be obtained if individual components were to be determined. Figure 3.8 illustrates the reconstructed ion current (RIC) full-scan mass spectra of a four-component mixture at 0.5 volume percent each, which corresponds to approximately 0.4 ng injected on the column. The signal-to-noise in the RIC was approximately 3, which represents the limit of detection for the HTA method. The sensitivities of the four components are given by the slope of the calibration curves illustrated in Figure 3.9. These sensitivities were determined in order to compare the results to the actual ASTM sensitivities in Table 5 of the ASTM D-2789 standard (6). Table 3.2 compares the sensitivities (slopes of the response curves in Figure 3.9) to the sensitivities of Table 5 of the ASTM standard (6), after normalization to the C9 paraffin (nonane). The results indicate that similar trends in sensitivities for the four components were observed for the two methods, although the propylbenzene sensitivity was significantly greater in the ASTM results.

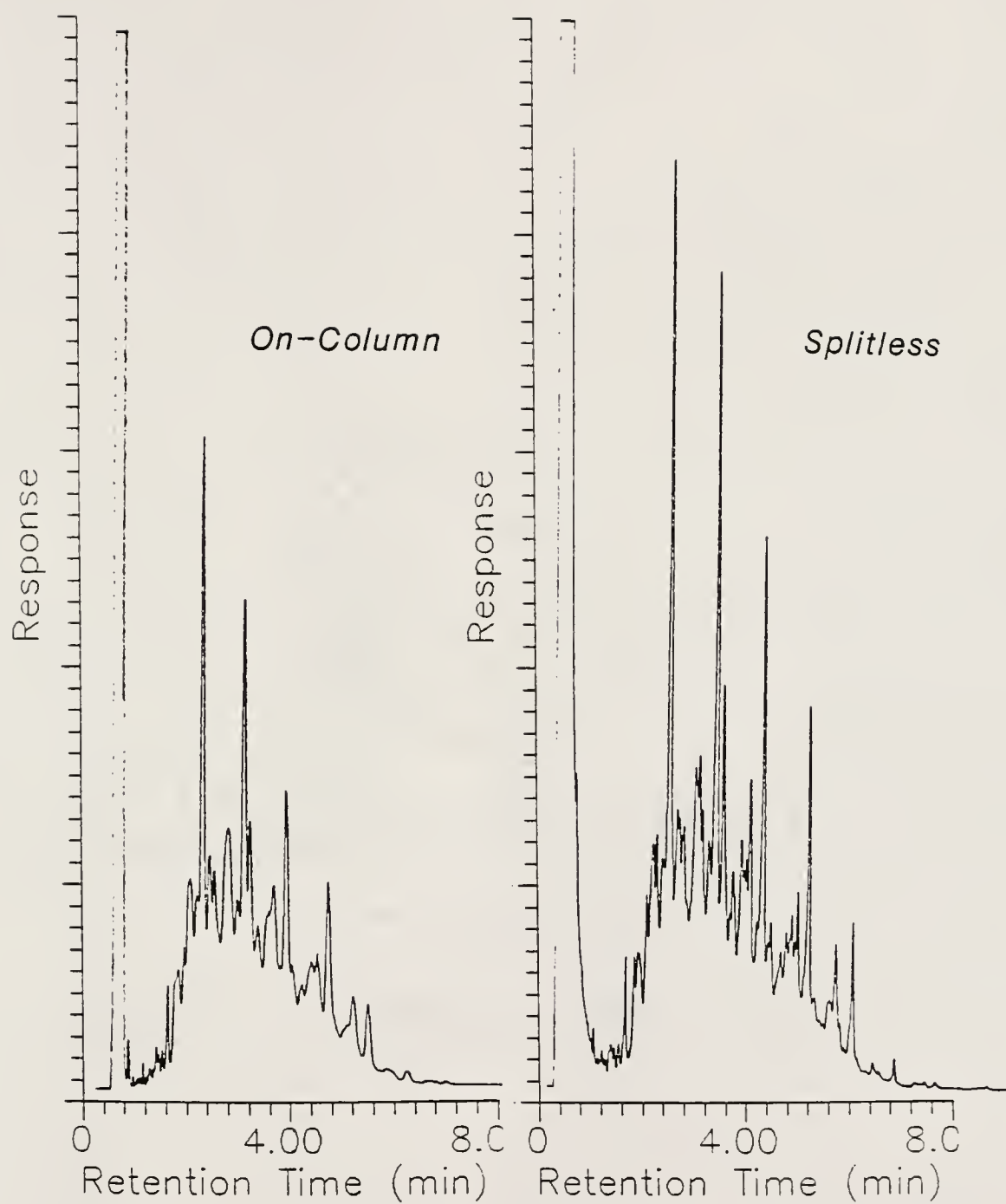


Figure 3.6. Chromatograms of JP-7 jet fuel on a 3 meter column comparing on-column and splitless injections.

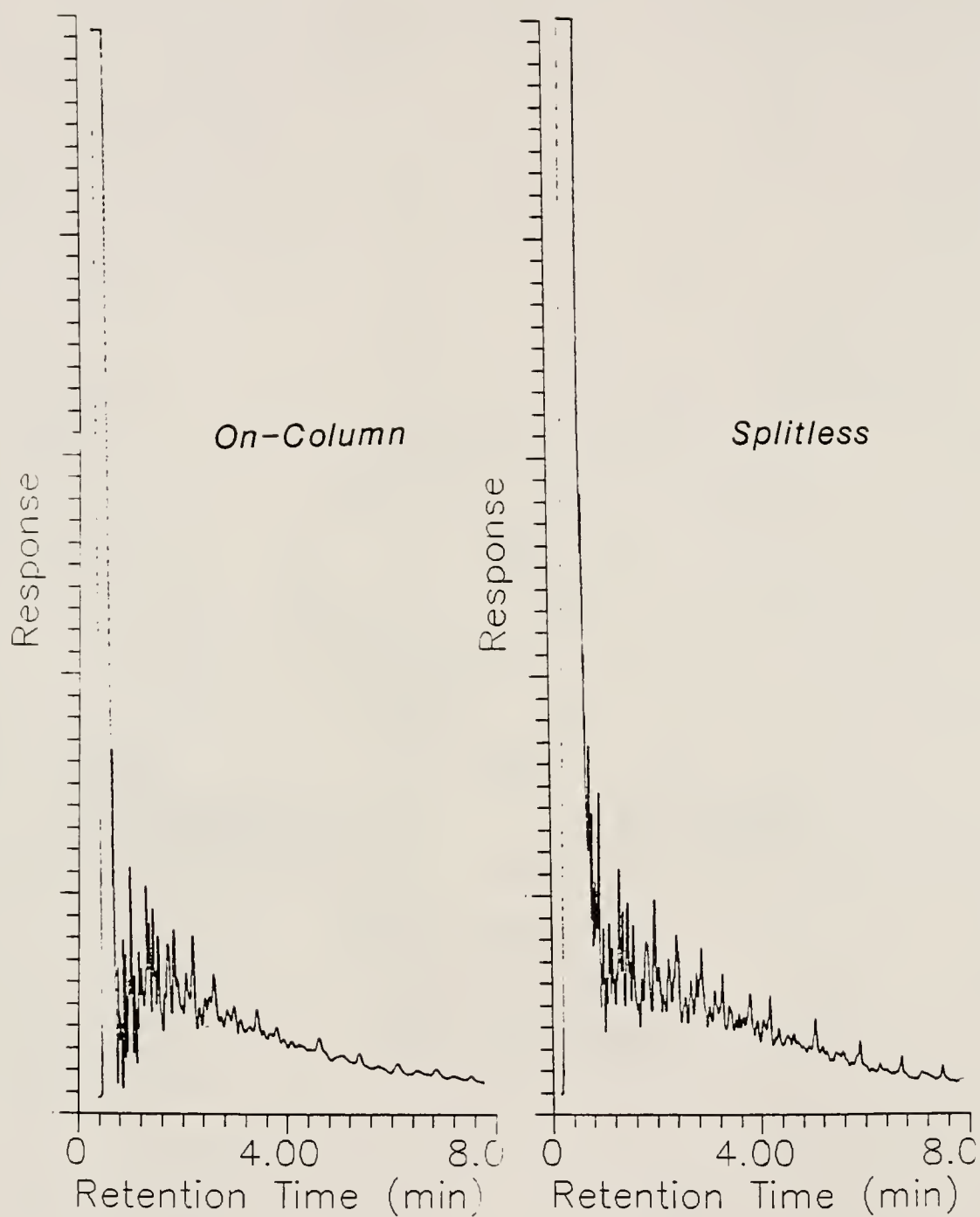


Figure 3.7. Chromatograms of JP-4 jet fuel on a 3 meter column comparing on-column and splitless injections.

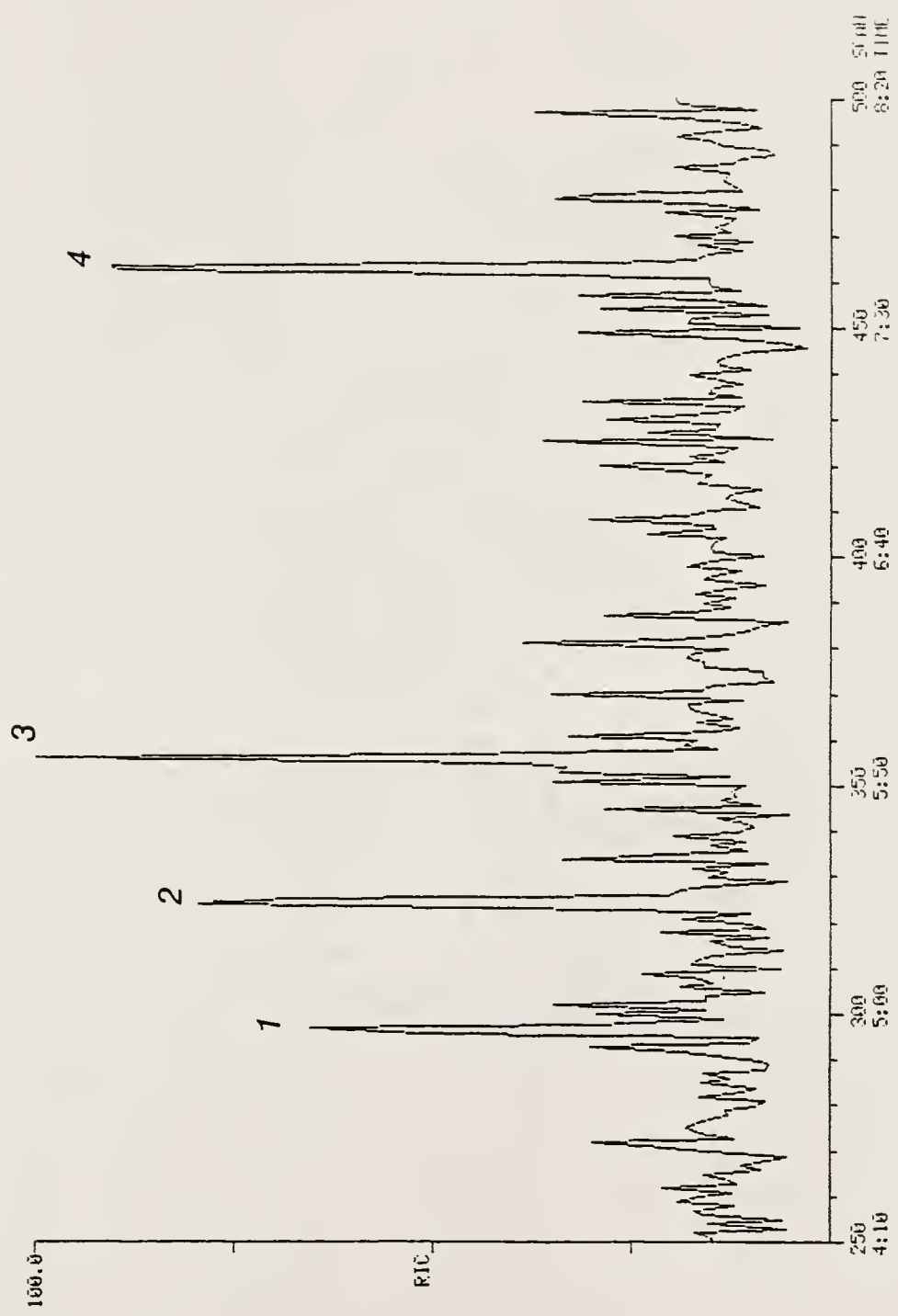


Figure 3.8. Chromatogram of nonane (1), cyclooctane (2), propylbenzene (3), and decalin (4) at 0.5 volume % each using 0.4 μ L split injection on a 3 meter column.

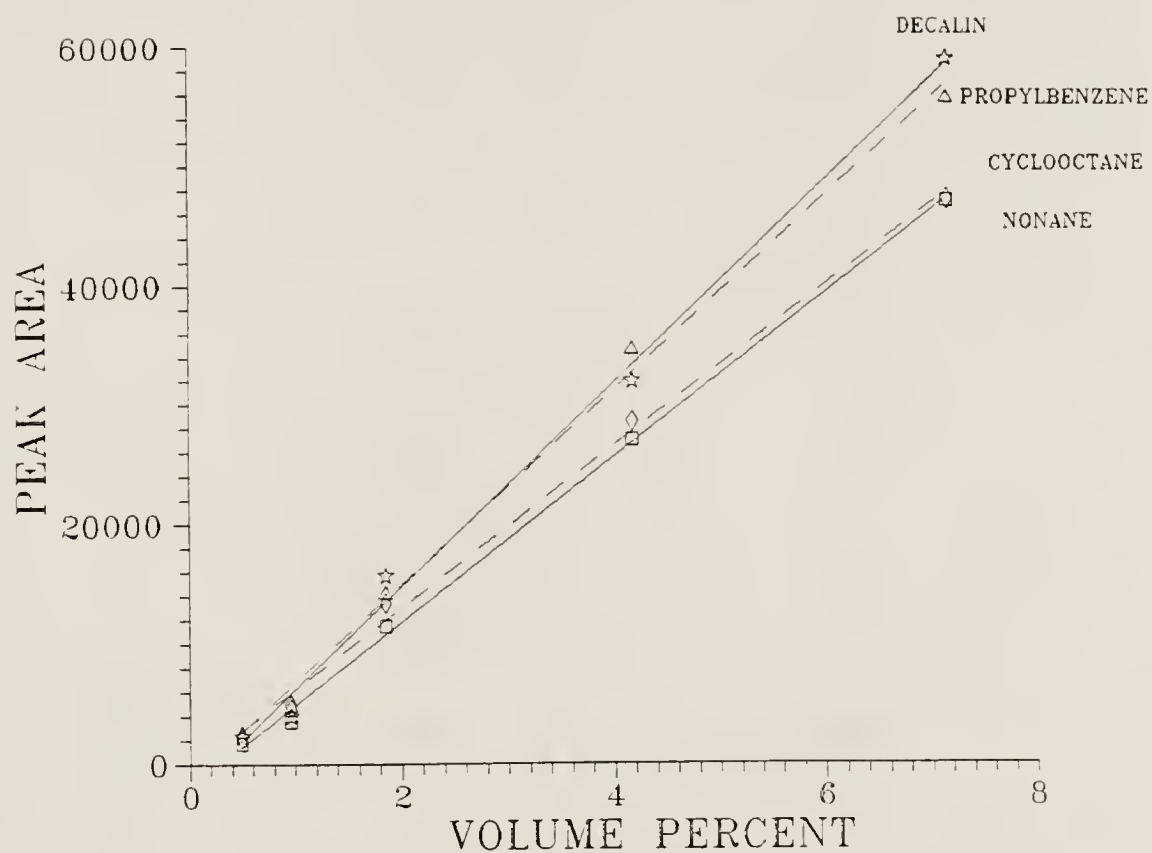


Figure 3.9. Response curve obtained by linear regression for nonane, cyclooctane, propylbenzene, and decalin at various volume percentages.

Table 3.2

Comparison of Sensitivities of ASTM and GC/MS/HTA
Results for a Four-Component Mixture
Normalized to the ASTM Sensitivity of Nonane
(Response per Volume %)

COMPONENT	ASTM SENSITIVITY	GC/MS/HTA SENSITIVITY
DECALIN	1.99	2.15
PROPYL- BENZENE	2.52	2.06
CYCLO- OCTANE	1.72	1.74
NONANE	1.72	1.72

The precision of the HTA method was determined by replicate analyses of several jet fuel samples. The precision was dependent upon the jet fuel analyzed or the composition of the fuels. The precision of the HTA method is summarized in Table 3.3, in which the average percent relative standard deviation is listed by hydrocarbon type for all fuels analyzed in replicate. The high average relative standard deviations were a result of that particular volume percent being very low. The dashed lines indicate a consistent result of zero volume percent.

Characterization of the GC/MS/HTA Method

Comparisons of ASTM and GC/MS/HTA Results

One of the major tasks in this research effort was to analyze a number of real jet fuel samples with the newly developed GC/MS/HTA method and to compare the results to those from the long-established ASTM D-2789 method. These comparisons would provide information on the validity of the ASTM inverse calibration matrices with GC sample introduction and quadrupole mass analysis. Table 3.4 shows these comparisons for five jet fuels. Several methods were used to evaluate trends in the comparison versus composition, but none could be found. The accuracy of the ASTM method has not been evaluated; therefore, the comparison does not necessarily reflect the accuracy of the GC/MS/HTA method.

Table 3.5 demonstrates the comparisons of several synthetically prepared jet fuels. The "recipe" results were calculated from the known volumes of the components added. Again these comparisons do not necessarily represent accuracy of the GC/MS/HTA method, since the

Table 3.3

The Average Relative Standard Deviation for the GC/MS/HTA of
all Replicate Analyses and Separate Jet Fuels

HYDROCARBON TYPE	AVERAGE OF ALL FUELS	JP-4 2455	JP-7	JP-8X 2414	JP-8X 2429
PARAFFIN	3.0	2.1	1.2	7.1	1.7
MONOCYCLO- PARAFFIN	3.8	2.5	0.6	6.8	5.3
DICYCLO- PARAFFIN	5.6	18.1	1.2	1.4	1.8
ALKYLBENZENE	7.6	3.8	18.8	2.5	5.4
INDANE/ TETRALIN	5.0	10.7	-	2.0	2.4
NAPHTHALENE	7.7	-	-	8.7	6.7
AVERAGE CARBON NUMBER					
AROMATIC	0.5	0.5	0.9	0.5	0.2
PARAFFIN	0.3	0.7	0.3	0.1	0.0

Table 3.4

Comparison of GC/MS/HTA and ASTM D-2789 Results
on Various Fuels, in Volume %

Fuel	Paraffin	Monocyclo- paraffin	Dicyclo- paraffin	Alkyl- benzene	Indane- Tetralin	Naphthalene	Aromatic C#	Paraffin C#
<u>JP-4 2455</u>								
GC/MS/HTA	61.5(.2)	18.5(.8)	3(1)	14.8(.9)	2.0(.4)	0	9.06(.07)	9.50(.08)
ASTM D 2789	70.8	18.0	2.1	7.6	1.4	0.1	8.69	8.01
<u>JP-8X 2429</u>								
GC/MS/HTA	0	3.2(.8)	68(2)	6.6(.7)	21.4(.8)	1.3(.3)	8.0(.1)	9.01(.01)
ASTM D 2789	1.3	21.5	56.0	7.2	13.1	0.9	8.14	8.91
<u>JP-8X 2414</u>								
GC/MS/HTA	7.0(.5)	10.3(.7)	35.0(.5)	15.7(.4)	29.7(.6)	2.3(.2)	9.87(.05)	9.40(.01)
ASTM D 2789	14.2	27.0	26.6	15.3	14.5	2.3	9.18	9.46
<u>JP-8X SIMULATED</u>								
GC/MS/HTA	11.5(.2)	17.0(.9)	54.9(.9)	7.4(.4)	8.5(.2)	0.6(.04)	8.53(.02)	9.00(0)
ASTM D 2789	12.1	23.1	58.7	2.9	4.1	0.2	7.65	8.69
<u>JET-A 2532</u>								
GC/MS/HTA	18.1	38.1	33.4	5.7	4.6	0	9.32	9.30
ASTM D 2789	27.4	44.7	20.8	4.9	2.1	0.2	8.41	8.86

Note: Numbers in parenthesis indicate the standard deviation n=3.

Table 3.5

Comparison of GC/MS/HTA Results and Synthetic Fuel Recipes
for Various Synthetic Fuels, in Volume %

Fuel	Paraffin	Monocyclo- paraffin	Dicyclo- paraffin	Alkyl- benzene	Indane- Tetralin	Naphthalene	Olefins
<u>JP-8X SIMULATED</u>							
GC/MS/HTA	11.5	17.5	54.9	7.4	8.5	0.6	-
RECIPE	12	20	60	(combined unsaturates 8 %)			
<u>HIGH AROMATIC</u>							
GC/MS/HTA	13.5	4.0	3.8	51.0	13.9	13.8	-
RECIPE	30	(combined 10 %)		45	10	5	-
<u>GRAND MIX</u>							
GC/MS/HTA	23.0	14.0	14.8	30.3	0.1	17.5	-
RECIPE	40	10	20	20	0.0	5	5
<u>ALL GROUPS</u>							
GC/MS/HTA	36.6	17.2	2.9	26.7	4.7	11.8	-
RECIPE	60	(combined 10 %)		17	3	5	5

synthetic mixtures were formulated from complex petroleum fractions (Exxon Corporation) such as Isopar C, G, and M (isoparaffinic and paraffinic mixtures), and Aromatic 100 and 150 (aromatic mixtures). These mixtures were obtained by simple fractionation and bulk separation techniques, and were not intended for analytical standards. Two of these mixtures were analyzed by GC/MS for specific group components. The Isopar M mixture contained significant amounts of cycloparaffinic components, with trace aromatics. The Aromatic 150 contained indanes and naphthalenes; the paraffin content was not determined. The monocycloparaffin recipe results of the olefin-containing fuels (Grand Mix and All Groups) agree better when the olefin content is added to the monocycloparaffin content. These two hydrocarbon types produce similar fragmentation patterns which tend to equate the two types under the HTA method. More details of the olefin/cycloalkane effects on the GC/MS/HTA method will be covered later in this chapter and in Chapter V.

Simple Mixture Analysis

Simple mixtures were used to evaluate the accuracy of the GC/MS/HTA method. Teeter states in his paper on high resolution mass spectrometry for 22 hydrocarbon type analysis (29) that no sample can be prepared which is complex enough to be a valid test for any HTA method. This "Teeter Rule," as it has become known in our laboratory, poses a real paradox for validation of these methods: any mixture which is complex enough to be a valid test of the HTA matrix calculation is too complex to be prepared. Certainly such a paradox is difficult for any analytical chemist to accept. These experiments were

designed to test this rule as well as to evaluate the accuracy of the GC/MS/HTA method. Table 3.6 shows the GC/MS/HTA results of a simple C6 mixture compared to the actual calculated volume percentages. The mixtures were prepared solely of C6 components. The results clearly indicate the inaccuracy in the analysis of such a simple sample, although the zero percent components are correctly identified and the aromatic average carbon numbers agree quite well. Table 3.7 shows the GC/MS/HTA results of a simple C10 mixture compared to the actual calculated volume percentages. In this case, better agreement was obtained for those types present as well as the zero percent types. The aromatic average carbon was well off the mark, yet the paraffin average carbon number was very close.

The next step was to evaluate a mixture which contained a spread in carbon numbers. Table 3.8 shows the GC/MS/HTA results of a simple C8-C9 mixture compared to the actual calculated volume percents. The results again indicated the inaccuracy of the method for simple mixtures, although the precision of the analysis was quite good, as indicated by the average percent relative standard deviation of 2.3% for replicate injections. Again, the average aromatic carbon numbers do not agree as well as the average paraffinic carbon numbers. Table 3.9 shows the GC/MS/HTA results of a simple C8-C10 mixture compared to the actual calculated volume percents. The monocycloparaffin volume percent was quite low, which resulted in a larger volume percent for the dicycloparaffin and the two other hydrocarbon types present. The average aromatic carbon number was low while the average paraffinic carbon number was high compared to the calculated results. This seems

Table 3.6
Comparison of HTA on a Simple C6 Mixture
With Actual Volume Calculated Results

HYDROCARBON TYPE	PREPARED BY VOLUME %	HTA VOLUME %
PARAFFIN	70.6	52.3
MONOCYCLO- PARAFFIN	17.6	23.7
DICYCLO- PARAFFIN	0.0	0.0
ALKYLBENZENES	11.8	24.0
INDANE/ TETRALIN	0.0	0.0
NAPHTHALENE	0.0	0.0
AVERAGE CARBON NUMBER		
AROMATIC	6.0	6.00
PARAFFIN	6.0	6.75

Simple C6 Mixture Make-up: Paraffin: 300 μ L hexane
 200 μ L 3-methylpentane
 100 μ L 2,2-dimethylbutane

 Monocyclo-
 paraffin: 100 μ L cyclohexane
 50 μ L methylcyclopentane

 Alkylbenzene: 100 μ L benzene

Table 3.7

Comparison of HTA on a Simple C10 Mixture
With Actual Volume Calculated Results

HYDROCARBON TYPE	PREPARED BY VOLUME %	HTA VOLUME %
PARAFFIN	33.3	29.8
MONOCYCLO- PARAFFIN	0.0	0.0
DICYCLO- PARAFFIN	33.3	35.8
ALKYLBENZENE	33.3	34.3
INDANE/ TETRALIN	0.0	0.0
NAPHTHALENE	0.0	0.0
AVERAGE CARBON NUMBER		
AROMATIC	10.0	8.44
PARAFFIN	10.0	9.96

Table 3.8

Comparison of HTA on a Simple C8-C9 Mixture
With Actual Volume Calculated Results

HYDROCARBON TYPE	PREPARED BY VOLUME %	HTA VOLUME %
PARAFFIN	44.5	39.2 (.5)
MONOCYCLO- PARAFFIN	33.4	21.3 (.2)
DICYCLO- PARAFFIN	0.0	6.9 (.07)
ALKYLBENZENE	13.9	17.1 (.4)
INDANE/ TETRALIN	8.3	15.4 (.9)
NAPHTHALENE	0.0	0.0
AVERAGE CARBON NUMBER		
AROMATIC	9.00	8.68
PARAFFIN	8.43	8.44

C8-C9 Mixture Composition (μ L)

C8: octane 50
2,5-dimethylhexane 50
2,3,4-trimethylpentane 20
octane 50
ethylcyclohexane 20

C9: nonane 50
2,2,5-trimethylhexane 20
isopropylcyclohexane 50
indane 30
propylbenzene 50

Table 3.9

Comparison of HTA on a Four-Component Mixture
With Actual Volume Calculated Results
(in Volume Percent)

HYDROCARBON TYPE	CALCULATED BY VOLUME	HTA EXPERIMENTAL
PARAFFIN	25	27.0
MONOCYCLO- PARAFFIN	25	9.8
DICYCLO- PARAFFIN	25	33.7
ALKYLBENZENE	25	29.2
INDANE/ TETRALIN	-	0.0
NAPHTHALENE	-	0.3
AVERAGE CARBON NUMBER		
AROMATIC	9.0	8.68
PARAFFIN	9.0	9.59

to be the normal trend for these simple mixtures. Table 3.10 shows the analysis of the same mixture as in Table 3.9 with the hexane solvent included in the HTA calculation. The changing HTA volume percent results generally agree with those expected, with the exception of the monocycloparaffin results, which increase rather than decrease. This would be expected since the mass spectrum of hexane contains a large relative abundance of m/z 41, which is an ion of the monocycloparaffin Σ -series. The average aromatic carbon number for the GC/MS/HTA results remains constant when hexane is included in the calculation, as it should. The average paraffinic carbon number decreases as expected and shows excellent agreement within the predicted value.

To summarize, the analysis of simple mixtures by GC/MS/HTA does not result in correct volume percent, which may simply be a verification of the Teeter Rule. The paraffin and alkylbenzene volume percents showed the best and most consistent agreement. The average paraffinic carbon numbers consistently showed the best agreement except for the simple C6 mixture. The average aromatic carbon number was consistently low compared to the actual results. The C10 mixture analysis was quite accurate, unlike the other two simple mixtures. This may be an erroneous result or may have some significance. Perhaps the sample make-up of the C10 mixture more closely matches that of the original C10 mixture used in the calibration matrix, or the matrix calculation works better for a more closely distributed (single carbon number) mixture distribution.

Table 3.10

Comparison of HTA on a Four-Component Mixture
 With Actual Volume Calculated Results
 With the Hexane Solvent Included in the Calculation
 (in Volume Percent)

HYDROCARBON TYPE	CALCULATED BY VOLUME	HTA EXPERIMENTAL
PARAFFIN	79	70.5
MONOCYCLO- PARAFFIN	7	16.2
DICYCLO- PARAFFIN	7	5.5
ALKYLBENZENE	7	7.7
INDANE/ TETRALIN	—	0.0
NAPHTHALENE	—	0.0
AVERAGE CARBON NUMBER		
AROMATIC	9.0	8.72
PARAFFIN	6.7	6.70

Sample Mixture in 1000 μL hexane:

100 μL	nonane
100 μL	cyclooctane
100 μL	n-propylbenzene
100 μL	decalin

Inverse Calibration Matrix Variation

An initial goal of this project was to validate the use of the existing (ASTM D-2789) inverse calibration matrix with quadrupole mass analysis. Since the matrix was prepared with one specific set of calibration mixtures, it was desired to determine the effect of calibration sample make-up on the inverse calibration matrix. A series of C6 components was used to prepare an inverse calibration matrix for carbon number 6 only. The hydrocarbon types were limited to paraffins, monocycloparaffins, and aromatics because there are no C6 members of the other types. Table 3.11 indicates the sample make-up used for the determination of each hydrocarbon type similarity coefficient in the inverse calibration matrix. The similarity coefficients are normalization factors for the mixing of mass spectral ions of the characteristic ion series. Various combinations were used for the inverse calibration matrix. The calculational method used is similar to that outlined in the experimental chapter. A computer program was written to calculate the C6 inverse calibration matrix based on the calculational method shown in Appendix A. A simple C6 mixture was prepared and analyzed using the various inverse calibration matrices. The results are compared to the actual volume calculated results in Table 3.12. The results show a significant amount of fluctuation, indicating the dependence of the calibration sample make-up on the matrix results. The closest agreement comes with the P4C2B1 combination, whose monocycloparaffin make-up is similar to the test mixture make-up but whose paraffin make-up is not. The worst agreement comes with the P4C1B1 combination, which is expected since the paraffin

Table 3.11

Component Codes and Make-Up for Preparation of Samples
Used in the Various Carbon Number 6 Inverse Calibration Matrices

Component Code		Sample Make-Up (in μL)		
Paraffins		hexane	3-methylpentane	2,2-dimethylbutane
P1		500	250	100
P2		250	100	500
P3		100	500	250
P4		1000	250	100
Monocyclo- paraffins		cyclohexane	methylcyclopentane	
C1		500	250	
C2		250	500	
Alkylbenzenes		benzene		
B1		1000		

Table 3.12

Comparison of Volume Percent Results on a Simple Carbon Number 6 Mixture Using the Various Combinations of Calibration Mixtures as Listed in Table 3.11 Previously Shown

Calibration Standard Composition by Component Codes	Paraffin	Monocyclo- paraffin	Alkylbenzene (benzene)
P1C1B1	74	10	16
P1C2B1	74	10	16
P2C1B1	67	19	14
P2C2B1	67	19	14
P3C1B1	68	18	15
P3C2B1	68	18	15
P4C1B1	53	36	11
P4C2B1	69	17	15
ACTUAL VOLUME CALCULATED	70.6	17.6	11.8
Simple C6 Mixture Make-up:	Paraffin:	300 μ L hexane 200 μ L 3-methylpentane 100 μ L 2,2-dimethylbutane	
	Monocyclo- paraffin:	100 μ L cyclohexane 50 μ L methylcyclopentane	
	Alkylbenzene:	100 μ L benzene	

and monocycloparaffin make-up is quite different from the test mixture make-up. The aromatic results, however, are in the closest agreement with this combination. This series of experiments illustrates the importance of the make-up of each single type component in determination of the similarity coefficients and the inverse calibration matrices. This C6 example represents the simplest case in this analysis. The complications faced with increasingly higher carbon number mixtures and matrices are unknown. The complexities of these mixtures may tend to eliminate these problems or enhance them.

Perturbation Jet Fuel Analysis

The GC/MS/HTA validation experiments described so far indicate that there still remains a need for validation of the GC/MS/HTA method since the above validation experiments contained limitations such as the Teeter Rule in the simple mixture analysis, and the unknown composition of the petroleum fractions in the synthetic fuel comparisons. To maintain the required complexity of the mixtures to be analyzed (to avoid complications due to the Teeter Rule), the jet fuels were perturbed by addition of a pure component of known volume. Table 3.13 shows the GC/MS/HTA results for a JP8X jet fuel before and after spiking the fuel with different amounts of various pure components. The paraffin volume percent of the first three spiked fuels should be increased to a calculated 28.6%. The fourth spiked fuel, which contains no paraffin spike, should agree with the "fuel only" results. These were in fact the results observed. The fuel containing the nonane and undecane spike showed the closest agreement. The volume

Table 3.13

Comparison of GC/MS/HTA of 86-POSF-2429 JP8X FUEL
After Spiking with Various Hydrocarbon Types
in Volume %

HYDROCARBON TYPE	FUEL	SPIKE 1*	SPIKE 2	SPIKE 3	SPIKE 4
PARAFFIN	0.0	29.6 (28.6)	24.6 (28.6)	32.0 (28.6)	0.2 (0.0)
MONOCYCLO- PARAFFIN	6.6	1.2 (4.7)	6.7 (4.7)	0.2 (4.7)	15.1 (19.0)
DICYCLO- PARAFFIN	72.5	53.8 (57.8)	52.0 (57.8)	52.2 (57.8)	52.0 (57.8)
ALKYLBENZENE	6.2	4.6 (4.4)	4.9 (4.4)	4.7 (4.4)	22.9 (18.7)
INDANE/ TETRALIN	14.4	10.6 (10.3)	11.6 (10.3)	10.4 (10.3)	9.3 (10.3)
NAPHTHALENE	0.3	0.2 (0.2)	0.2 (0.2)	0.4 (0.2)	0.5 (0.2)
AVERAGE CARBON NUMBER					
AROMATIC	7.50	7.32	7.53	7.48	8.53
PARAFFIN	9.02	9.35	8.55	9.51	9.01

*

SPIKE 1: 500 μ L FUEL + 100 μ L n-nonane + 100 μ L undecane

SPIKE 2: " + 200 μ L n-octane

SPIKE 3: " + 200 μ L n-decane

SPIKE 4: " + 100 μ L butylbenzene + 100 μ L cyclooctane

Note: numbers in parenthesis indicate the expected results due to dilution or addition of that specific type.

percent of the remaining hydrocarbon types of the first three spiked fuels (paraffinic spikes) should decrease due to dilution and remain relatively constant. The calculated values are monocycloparaffin, 4.7%; dicycloparaffin, 51.8%; alkylbenzenes, 4.4%; indane/tetralin, 10.3%; and naphthalene, 0.2%. On examination of Table 3.13, excellent agreement is observed for all types for the first three spikes, with the exceptions of the monocycloparaffin results. Attempts were made to explain this behavior by analysis of the mass spectra of each particular component, but no distinctions could be made. Most paraffins contain a large relative abundance of m/z 41 (30-50%) and m/z 55 (5-15%) which are ions indicative of the monocycloparaffin type. The fourth spiked fuel also demonstrates excellent agreement with the calculated perturbations for the hydrocarbon types not present in the spike. The monocycloparaffin results were low compared to the calculated (19.0%), and the alkylbenzene was high compared to the calculated (18.7%). Again no explanation could be drawn by examination of the component spectra; however, the sum of the two types (monocycloparaffin and alkylbenzene) did equal the sum of the calculated results. The average carbon numbers demonstrated good correlation with the perturbation of the fuel. The average aromatic carbon number remained relatively constant for paraffin perturbation but increased with the butylbenzene (C10) addition. The average paraffinic carbon number also correlated with the paraffin perturbation: 9.35 for nonane and undecane (C10 average) addition; 8.55 for octane addition; 9.51 for decane addition; and no change with the addition of spike number four.

This perturbation approach appears to be a much more successful approach for validation of the GC/MS/HTA method than the previous two methods (simple mixture analysis and ASTM comparisons). The much better agreement seems to further support the "Teeter Rule" and indicates that additional experiments should be performed.

A second set of fuel perturbation experiments was performed using the standard addition method. Figure 3.10 illustrates the GC/MS/HTA results for standard addition of n-propylbenzene to JP-4 2455 jet fuel. The HTA aromatic type response was compared to the theoretical aromatic type response of the volume percent added. The more positive slope of the experimental line indicates that upon increased additions of n-propylbenzene to the jet fuel an above-average GC/MS/HTA aromatic response will result. However, the negative x-intercept (-13.2 aromatic volume percent), which indicates the volume percent of the original fuel, agree to within experimental error with the original HTA result (12.8). To test the hypothesis stated above in regard to the above average GC/MS/HTA response of the n-propylbenzene alkylbenzene, the same fuel was spiked with the Aromatic 150 mixture. Figure 3.11 illustrates the results of this standard addition experiment. The "real line" intersects with the theoretical line and adheres more closely to it in the region of the data points. This confirms the above average response hypothesis of the n-propylbenzene. This may indicate that the Aromatic 150 better represents the composition of the original calibration solution used in the preparation of the inverse calibration matrix. The larger negative x-intercept of the Aromatic 150 indicates that a larger volume percent must be added to equal the

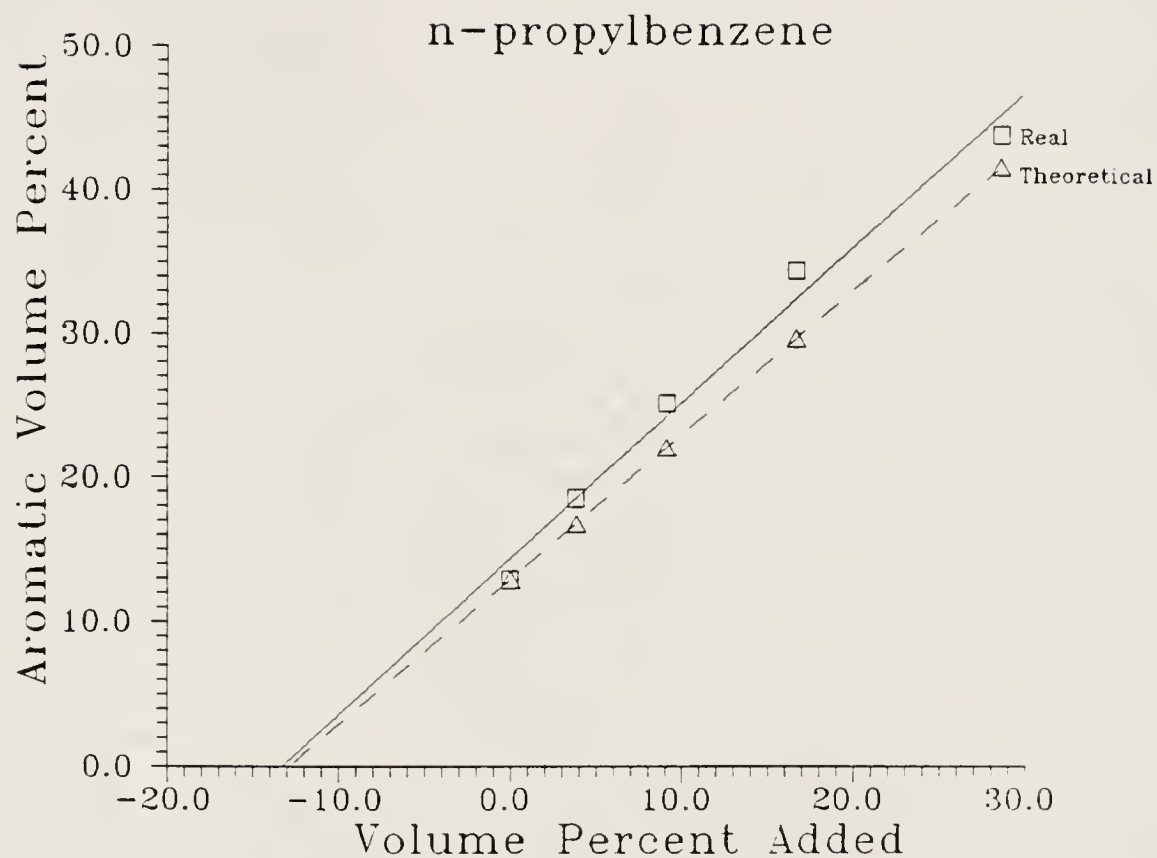


Figure 3.10. Plot of volume percent standard addition of n-propylbenzene to jet fuel JP-4 2455. The real line indicates the experimental results.

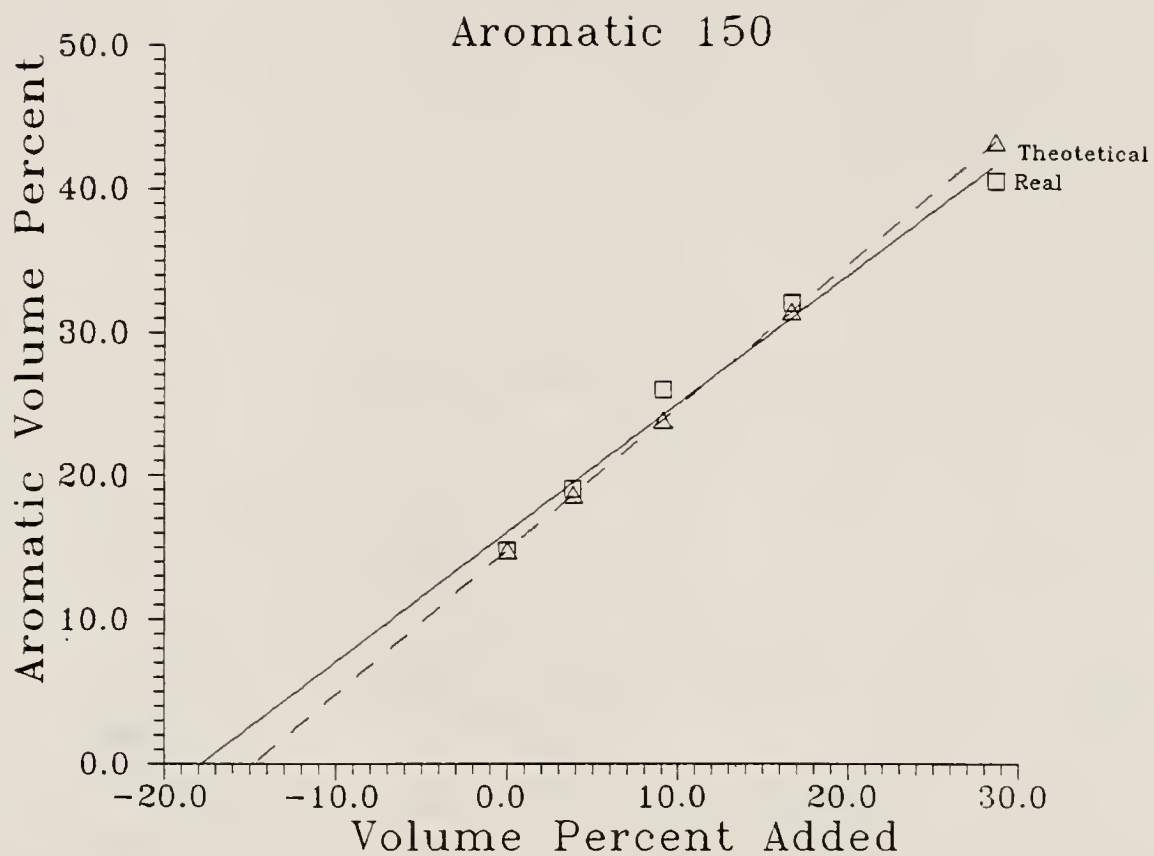


Figure 3.11. Plot of volume percent standard addition of Aromatic 150 to jet fuel JP-4 2455. The real line indicates the experimental results.

theoretical volume percent. This result is consistent with the composition of the Aromatic 150 mix which is known to contain components other than alkylbenzenes such as indanes, tetralins, and naphthalenes. Figure 3.12 compares the mass spectrum of n-propylbenzene and the average mass spectra of the Aromatic 150 mixture. The presence of non-alkylbenzene aromatics in the Aromatic 150 is evident by the presence of m/z 117 and m/z 118, indanes and tetralins; m/z 128 and m/z 142, naphthalenes.

The above analysis of the standard addition plots was formulated based on the linear regression of the experimental standard additions. This seems appropriate when considering the linear theoretical plots; however, in both cases there was a clear curvature to the data points. This effect is illustrated in Figure 3.13 in which the experimental n-propylbenzene data have been connected by a spline fit. The decreasing slope with increasing volume percent added could possibly be explained by the partial molal volume of mixing theory, but the degree of change is much too large. The more negative x-intercept which was obtained in both of the previous results is not consistent with the types of additions made and otherwise has no explainable significance. These results confirmed the original linearization assumptions used above.

Evaluation of Olefin and Cycloparaffin Isomers

A major concern of the ASTM and GC/MS/HTA methods is the presence of olefins and how they effect the results of the monocycloparaffin volume percentages. In the ASTM method it is assumed that there is no difference between the fragmentation pattern of any two olefinic or cycloparaffin isomers of equal carbon number. This results in an

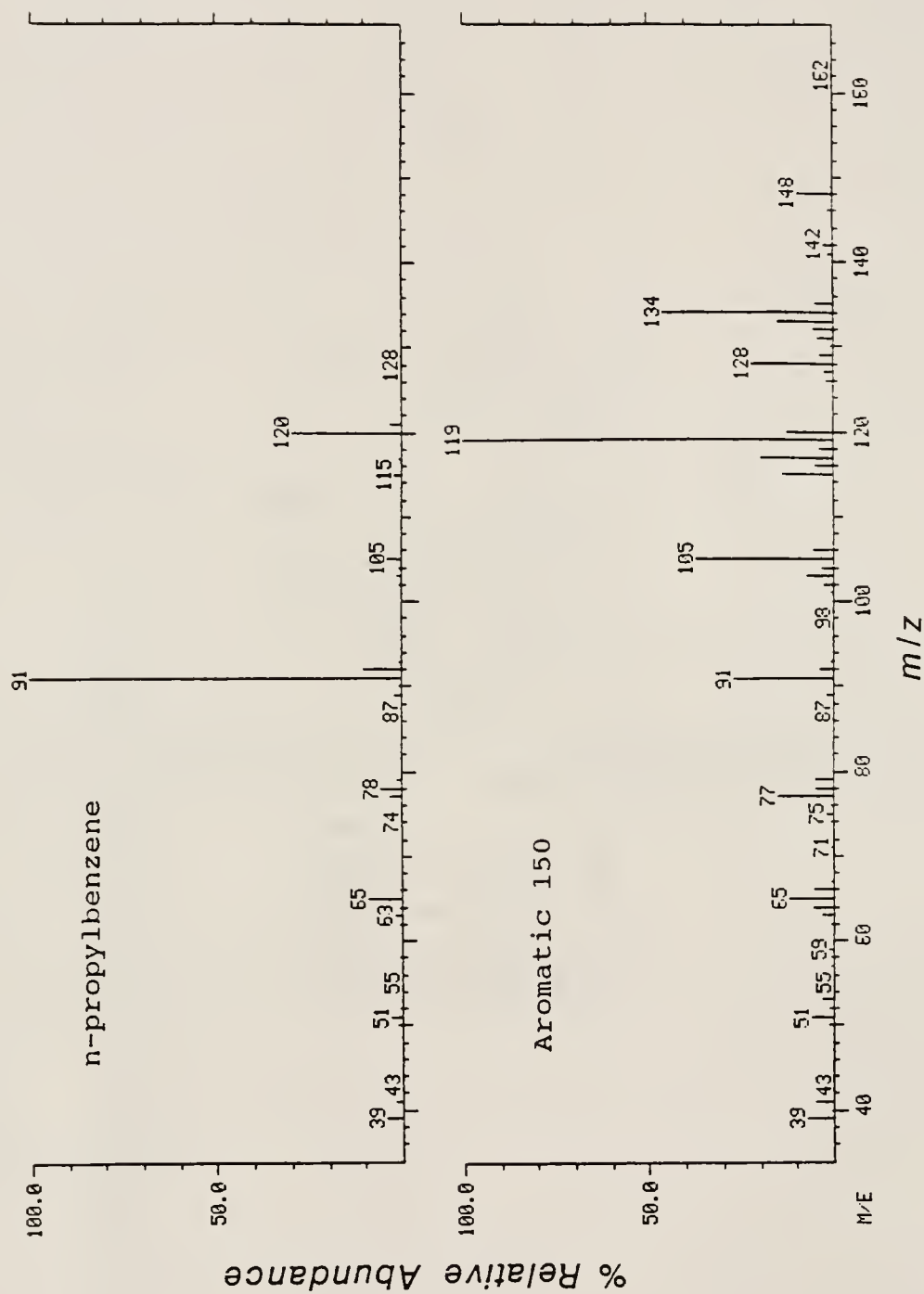


Figure 3.12. Mass spectra of n-propylbenzene and Aromatic 150.

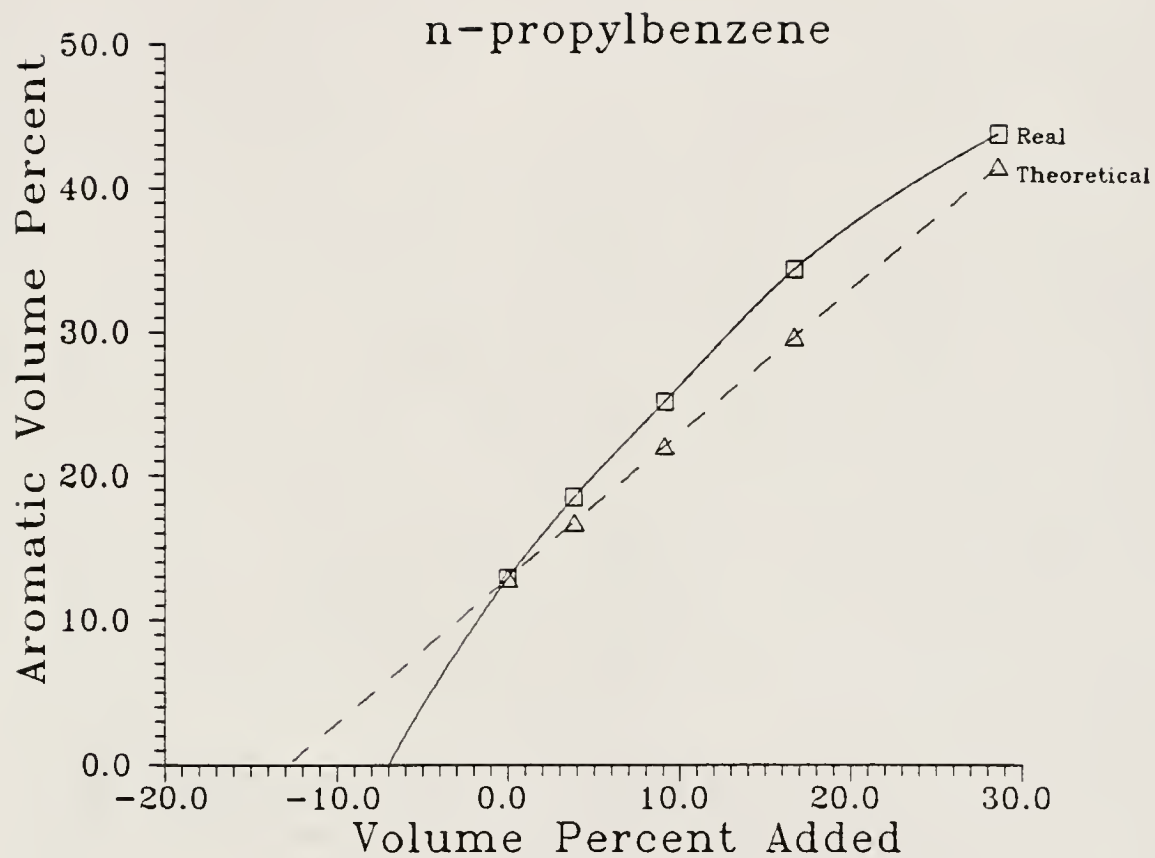


Figure 3.13. Spline fit to experimental volume percent standard addition of n-propylbenzene to jet fuel JP-4 2455 compared to theoretical addition.

uncertainty in the HTA analysis if the presence of olefins is uncertain or if their concentrations are unknown. The ASTM procedure requires the subtraction of the olefin volume percent from the monocycloparaffin volume percent when the olefin content is known. The olefin content may be determined using the ASTM D-875 standard method. We were interested in evaluating the effects of the olefin content on the GC/MS/HTA results and how they would compare to the isomeric monocycloparaffin content. Table 3.14 shows the differences in the GC/MS/HTA paraffin, monocycloparaffin, and dicycloparaffin results for the JP-4 2455 jet fuel after the addition of C7, C9, and C10 olefin and monocycloparaffin isomers. It should be noted that the C10 case was analyzed on a separate day which resulted in a slight variation in the "FUEL ONLY" results. The table also compares these results to the theoretical content expected. The results of the unsaturated hydrocarbon types are not shown since changes were incurred only through dilution. In all cases, the monocycloparaffin demonstrated a larger increase in the monocycloparaffin content than the olefin. Examination of the paraffin and dicycloparaffin content after perturbation of the fuels demonstrates some interesting results which can be evaluated in terms of the differences in the mass spectra of each and reference to the characteristic ion series for each hydrocarbon type (Table 2.1). Figure 3.14 shows the mass spectra of the C7 isomers cycloheptane and 1-heptene. A larger relative abundance of molecular ion (m/z 98) and $[M-15]^+$ (m/z 83) was obtained for the cycloheptane but produced little differences between the GC/MS/HTA results. Figure 3.15 shows the mass spectra of the C9 isomers

Table 3.14

Comparison of HTA of JP-4 2455 Jet Fuel
After Spiking with C7, C9, and C10 Cycloalkane and Olefin Isomers
(in Volume Percent)

HYDROCARBON TYPE	FUEL ONLY 500 μ L	Fuel+50 μ L cycloheptane	Fuel+50 μ L 1-heptene	Expected Result
PARAFFIN	61.5	57.9	59.9	55.9
MONOCYCLO- PARAFFIN	18.5	24.8	22.2	25.9
DICYCLO- PARAFFIN	3.1	1.1	1.8	2.8
HYDROCARBON TYPE	FUEL ONLY 500 μ L	Fuel+50 μ L propylcyclohexane	Fuel+50 μ L 1-nonene	Expected Result
PARAFFIN	61.5	55.1	61.4	55.9
MONOCYCLO- PARAFFIN	18.5	24.5	22.3	25.9
DICYCLO- PARAFFIN	3.1	6.4	1.4	2.8
HYDROCARBON TYPE	FUEL ONLY 500 μ L	Fuel+50 μ L iso- butylcyclohexane	Fuel+50 μ L 1-decene	Expected Result
PARAFFIN	58.8	52.2	58.3	53.4
MONOCYCLO- PARAFFIN	17.8	27.4	21.4	25.3
DICYCLO- PARAFFIN	4.0	3.7	3.4	3.6

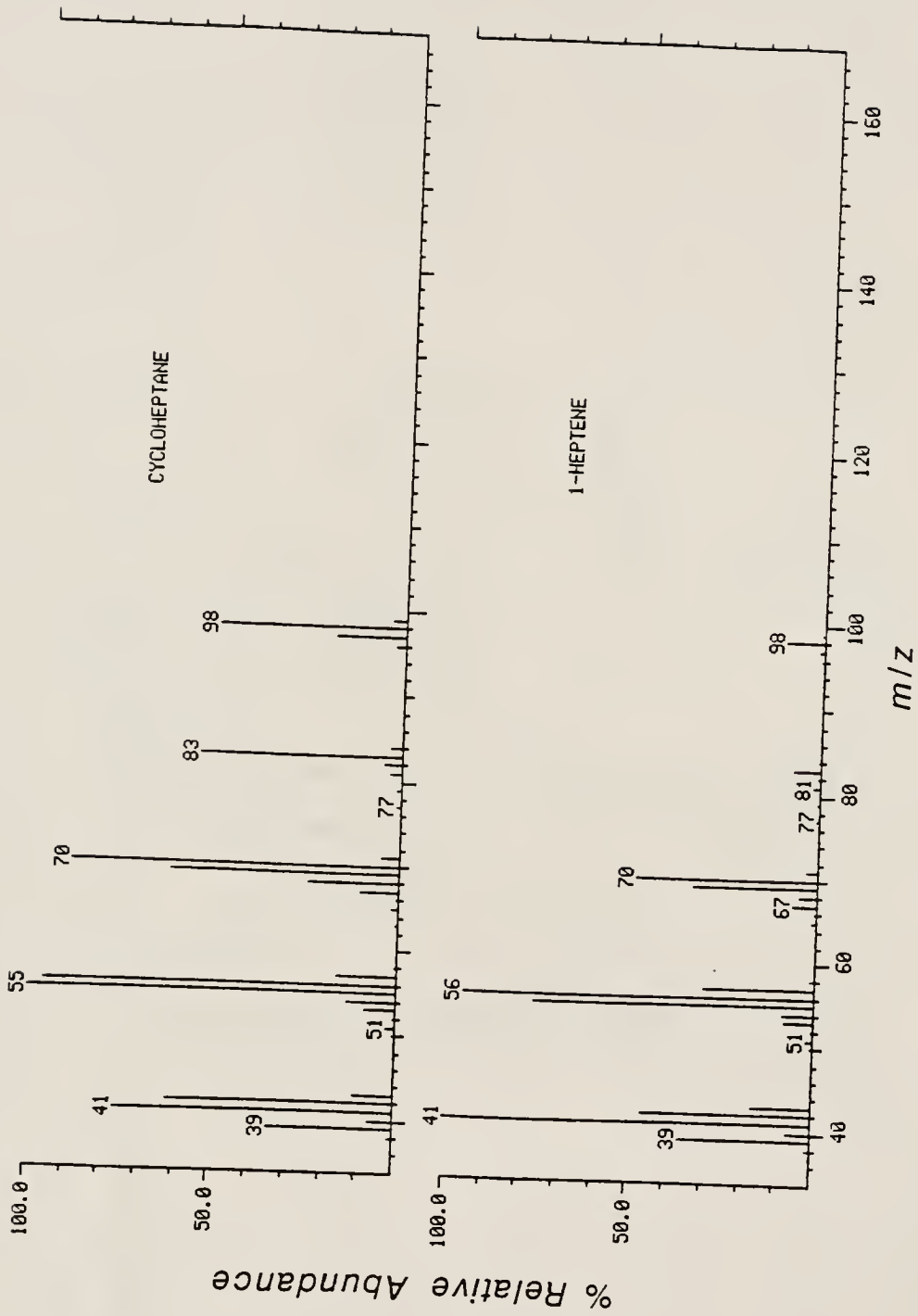


Figure 3.14. Comparison of mass spectra of C7 isomers cycloheptane and 1-heptene.

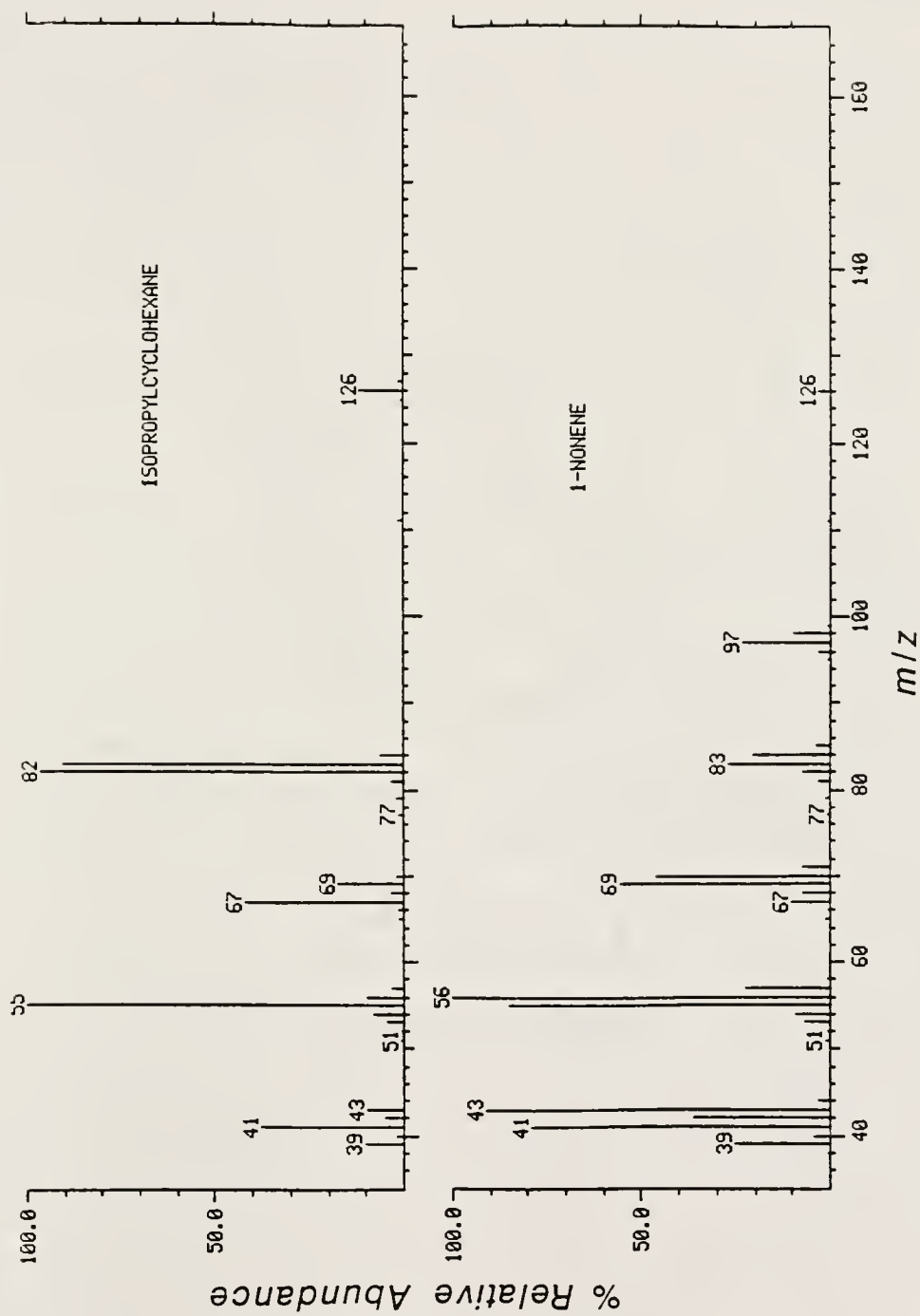


Figure 3.15. Comparison of mass spectra of C9 isomers isopropylcyclohexane and 1-nonene.

isopropylcyclohexane and 1-nonene. Again a larger relative abundance of molecular ion (m/z 126) was obtained for the cycloparaffin, but also the fragmentation pattern was quite different than that of the olefin. The large relative abundances of the m/z 82 fragment (96%) and the m/z 67 fragment (42%) for the cycloparaffin isomer, which were very low for the olefin (9%), caused the dicycloparaffin volume percent of the cycloparaffin-spiked fuel determined by HTA to be high. Similarly the large relative abundances of paraffinic fragment ions (m/z 43, 57, and 71) for the olefin isomer caused the paraffin volume percent of the olefin-spiked fuel to be well above that of the cycloparaffin-spiked fuel. Figure 3.16 shows the mass spectra of the C10 isomers isobutylcyclohexane and 1-decene. Again a larger relative abundance of molecular ion (m/z 140) was obtained for the cycloparaffin. The fragmentation patterns, although different, both contributed response to the dicycloparaffin volume percent of the spiked fuels. The slightly higher volume percent calculated for the cycloparaffin-spiked fuel was due to the larger relative abundance of m/z 82 fragment. The paraffinic volume percent was again larger for the olefin spiked fuel because of the large relative abundances of the paraffinic fragment ions, especially m/z 43.

These studies validate the need for separate determinations of cycloparaffin and olefin content in the HTA of jet fuels. New complications have been introduced as to the effects on the HTA calculated paraffin and dicycloparaffin content. Examination of the differences in the mass spectra of the isomeric monocycloalkanes and

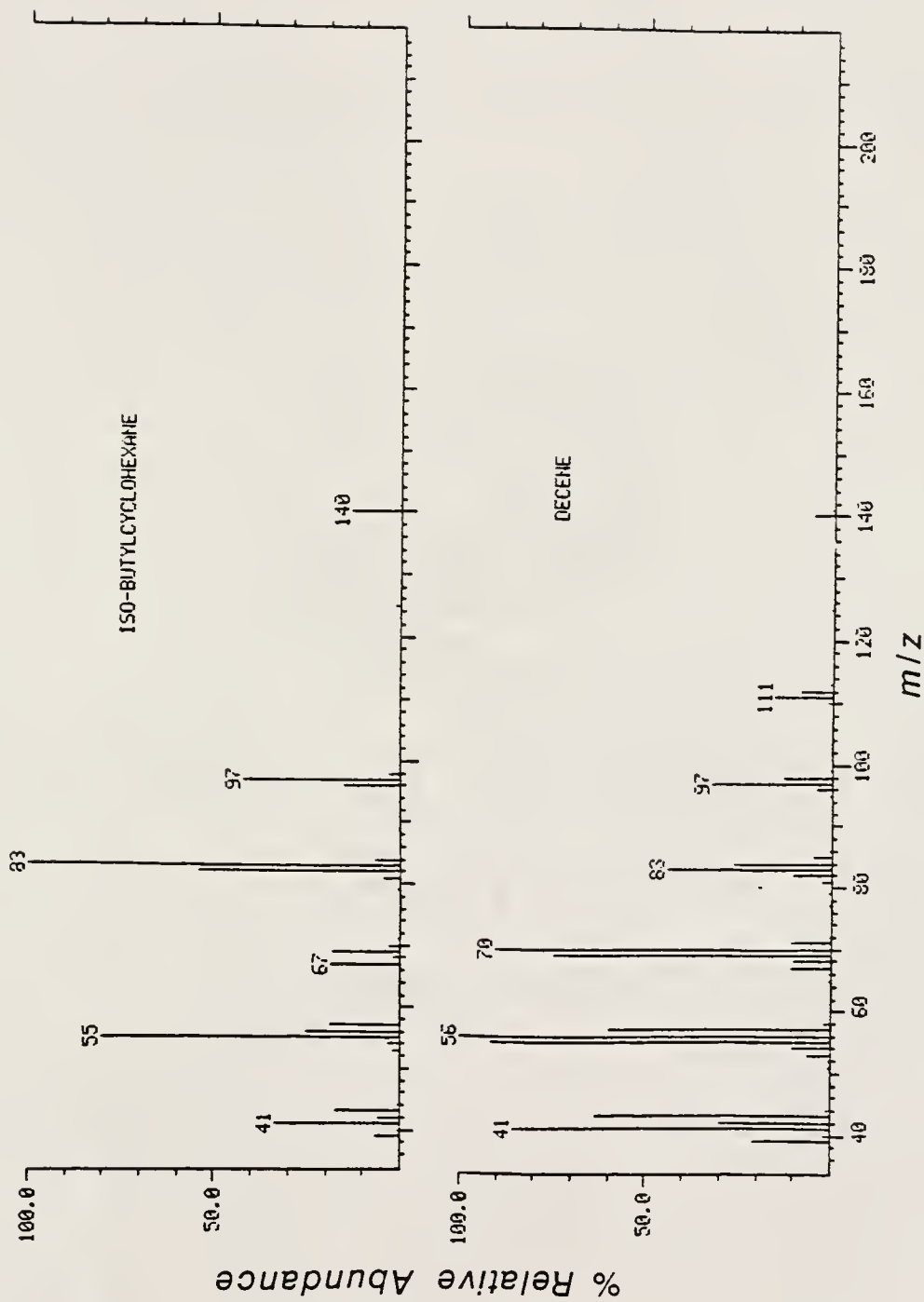


Figure 3.16. Comparison of mass spectra of C10 isomers isobutylcyclohexane and decene.

olefins of the three carbon numbers studied suggest the possibility of developing techniques which could identify and quantitate each isomer separately in the presence of the other.

Evaluation of Methods for Average Carbon Number Determinations

The GC/MS/HTA method relies heavily on the accuracy of the average carbon number calculations, since the inverse calibration matrices chosen are dependent upon these results. As in the ASTM methods, these average carbon numbers (aromatic and paraffinic) are determined based on the intensities of the paraffin and alkylbenzene molecular and fragment ion series such as $[M-15]^+$. This has raised a certain degree of speculation concerning the accuracy of this method. First, as mentioned, the method is based on the intensities of molecular and fragment ions, which are generally of very low relative abundance. This is particularly true for paraffins, whose molecular ion relative abundances are on the order of 1-5%. Alkylbenzenes, however have relatively abundant molecular ions, on the order of 20-50%. Therefore less error would be expected for the aromatic results. Second, the volume percent results of the remaining hydrocarbon types are dependent upon the average carbon number results of the paraffins and alkylbenzenes. For example, the dicycloparaffin volume percent is calculated based on the inverse calibration matrix determined by the average paraffin carbon number. This would obviously cause even greater error in the results for those samples which contain small amounts of paraffins relative to the dicycloparaffins. To clarify some of these uncertainties, a new method of calculating the average carbon numbers of a jet fuel was developed.

As was shown in Figure 2.2, the GC/MS simulated distillation (GC/MS/SD) method determines the centroid of the total area of a chromatographic profile. The GC/MS facilitates the ability to profile an ion series characteristic of a certain hydrocarbon type with an ion summation chromatogram, which may then be compared to a similar chromatogram of a homologous series of that hydrocarbon type. Figure 3.17 again illustrates this method, only in this case showing the paraffin series ($\Sigma 43$) of the JP-8X fuel with the corresponding n-paraffin homologous series in parallel. Several variations in this technique were used for the determination of the average carbon numbers. These variations were obtained by variations in the particular set of ions used in the ion summation chromatograms. Table 3.15 shows the results of these carbon number determinations for several jet fuels. From this table, three comparisons can be made for both aromatic and paraffinic average carbon numbers: comparison between the two GC/MS/SD methods (which will be explained below); comparison between the two GC/MS/SD methods and the GC/MS/HTA method; and comparison between the GC/MS/HTA and the ASTM method.

GC/MS Simulated Distillation

Table 3.15 provides data for the comparison of the two GC/MS/SD methods, SIM DIST #1 and SIM DIST #2 for both aromatic average carbon numbers and paraffinic average carbon numbers. The comparisons demonstrate the variations which were due to the characteristic set of ions used in the calculations as discussed above. The methods used for the two GC/MS/SD average carbon numbers determinations were as follows: the SIM DIST #1 method calculates the paraffinic carbon number based

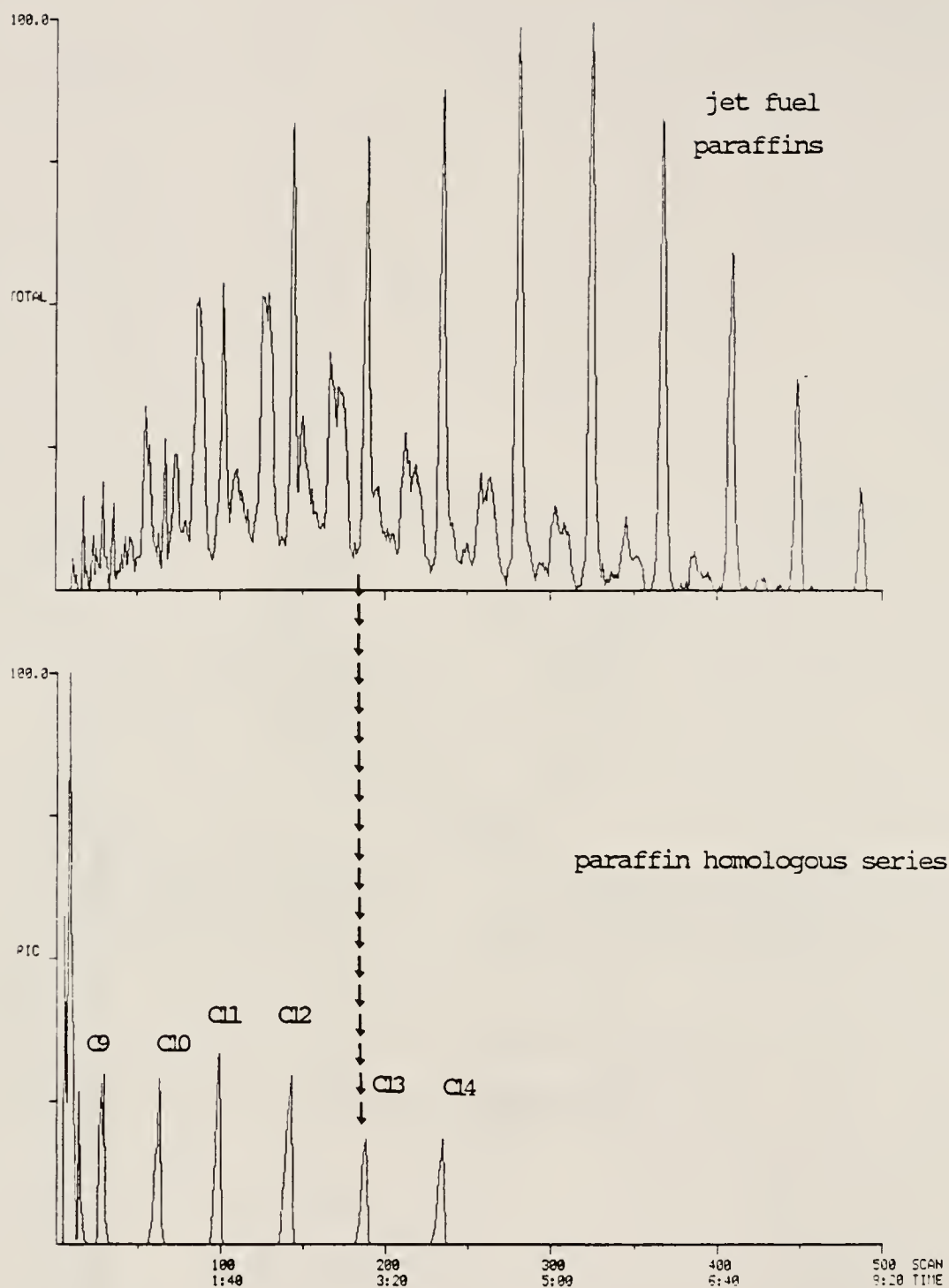


Figure 3.17. The paraffinic ($\Sigma 43$) ion summation chromatogram of jet fuel JP-8X 2414 on a 3 meter DB5 column. The centroid of the total area, indicated by the arrows, is referenced to the n-paraffin homologous series. The average paraffinic carbon number is calculated to be 12.89.

Table 3.15

Comparison of Average Paraffin and Aromatic Carbon Numbers
for Various Fuels Using Several Calculational Techniques

Fuel	<u>Aromatic Average Carbon Number</u>		ASTM	<u>Paraffin Average Carbon Number</u>		
	SIM DIST #1 ^a	SIM DIST #2 ^b		SIM DIST #1 ^a	SIM DIST #2 ^b	ASTM
JP-4 2455	10.4(.4)	10.9(.2)	8.69	12.1(.2)	9.50(.08)	8.01
JP-8X 2429	12.1	10.7	8.0(.1)	14	11.1	8.91
JP-8X 2414	10.9	11.9	9.87(.05)	13.1	11.8	9.46
JP-8X SIMULATED	10.2	10.7	8.53(.02)	12.4	11.1	8.69
JET-A 2532	11.8	11.8	9.32	12.6	12.5	8.86
JP-7 NARROW B.P. RANGE	11.6(.1)	11.85(.01)	10.5(.1)	12.4(.2)	11.52(.03)	-
PETROLEUM JP-8 2400	10.1	10.3	9.51	10.8	10.6	-
PETROLEUM JP-4 0988	9.9	10.2	9.16	10.7	10.8	-

^a SIM DIST #1 Area centroid based on paraffin and alkylbenzene ion summation chromatograms.

^b SIM DIST #2 Area centroid based on saturates and unsaturates ion summation chromatograms.

Note: Numbers in parenthesis are standard deviations.

solely on the ion summation chromatogram of the $\Sigma 43$ ions (paraffin), and the aromatic carbon number based on the ion summation chromatogram of the $\Sigma 77$ ions (alkylbenzene); the SIM DIST #2 method calculates the paraffinic carbon numbers based on the ion summation chromatogram of all the saturated ion sets, $\Sigma 43$, $\Sigma 41$, and $\Sigma 67$, (paraffin, monocycloparaffin, and dicycloparaffin), and the aromatic carbon numbers based on the ion summation chromatograms of all the unsaturated ion sets, $\Sigma 77$, $\Sigma 103$, $\Sigma 128$, (alkylbenzene, indane/tetralin, and naphthalene). To make a proper evaluation of these results, reference must be made to the composition of these jet fuels, as shown in Table 3.4. For those fuels whose saturated and unsaturated compositions were made up mainly of paraffins and alkylbenzenes, respectively, there were only small differences between the average carbon numbers obtained by two techniques. For example, the JP-4 2455 jet fuel has a saturated fraction composed mainly of paraffin, which results in little difference between the average paraffinic carbon numbers from the two techniques, 12.1 and 12.0. The JP-8X 2429 jet fuel, on the contrary, has a saturated fraction composed mainly of dicycloparaffin which has resulted in a large difference between the average paraffinic carbon numbers of the two techniques, 14 and 11.1. For this fuel the same trend was observed for the average aromatic carbon numbers, 12.1 and 10.7, since the unsaturated fraction was composed mainly of indane/tetralin rather than alkylbenzenes. In summary these two techniques of average carbon numbers determinations demonstrate a large dependency upon the composition of the jet fuel, which demonstrates the failures of the present ASTM method and the need for more specific

methods for carbon number determinations of each particular hydrocarbon type. These conclusions are further supported by the second set of comparisons between the GC/MS/SD and GC/MS/HTA results.

Comparison Between GC/MS/SD and GC/MS/HTA

Table 3.15 provides data for the comparison of the GC/MS/SD and GC/MS/HTA methods of average carbon number determination. The original purpose of the development of the GC/MS/SD method was to demonstrate the dependence of the average carbon number results on the sample concentration, and the limitations of calculating the paraffinic (saturated) and aromatic (unsaturated) average carbon number based on the paraffin and alkylbenzene composition only (both discussed above). The large differences between the GC/MS/SD and GC/MS/HTA results were not expected. In all cases a larger average carbon number (sometimes larger by 3 or 4 carbons) was obtained for the GC/MS/SD results than for the GC/MS/HTA results. This raised uncertainty in the results of the GC/MS/SD technique, although the simulated distillation methods seemed scientifically sound and much more tangible than the mass spectral technique of the GC/MS/HTA method discussed above. Consultation with the engineers at the Pratt and Whitney Fuels Division, who have analyzed many jet fuels for average boiling point by the ASTM simulated distillation method (44,45), suggested a consistent underestimation of the average carbon numbers by the ASTM D-2789 method.

Comparison Between GC/MS/HTA and ASTM

The final set of comparisons made in Table 3.15 were between the GC/MS/HTA and ASTM D-2789 results. These results were determined based

on the same computational technique as discussed at the beginning of this section. Large deviations between the results of the two techniques were apparent for most fuels, with the GC/MS/HTA values generally larger. The results of jet fuel JP-8X 2429 showed the best paraffinic and aromatic average carbon number agreement, while jet fuel JP-4 2455 showed the worst. The measure of paraffinic carbon number agreement may be correlated to the saturate composition of the fuels (see Table 3.4), since the JP-8X fuels (such as 2429 and 2414) were composed mainly of dicycloparaffins, and the JP-4 fuel was composed mainly of paraffins. These correlations are of course dependent upon the accuracy of the volume percent results, which are themselves dependent upon the average carbon number results. No correlation between the composition of the jet fuels and the aromatic carbon numbers could be determined. However, agreement between the two methods was generally better for the aromatic carbon numbers than for the paraffinic carbon numbers. This may be due to the increased accuracy of the technique as reflected in the larger relative abundance of the alkylbenzene molecular ions, as discussed above.

The presence of large amounts of naphthalenes in jet fuels can cause a large amount of error in the paraffinic average carbon number and ultimately in the final volume percent results (6), since the m/z 128, m/z 142, and m/z 156 ions used in the ASTM average paraffinic carbon number determination correspond to abundant molecular ions of naphthalene, methylnaphthalene, and dimethylnaphthalene, respectively. Investigations of the effect of this perturbation were made by spiking the JP-4 2455 jet fuel with dimethylnaphthalene. Table 3.16

Table 3.16

Comparison of GC/MS/HTA of JP4 Fuel
After Spiking with Dimethylnaphthalene
in Volume Percent

HYDROCARBON TYPE	FUEL ONLY 500 μ L	Fuel+100 μ L Dimethylnaphthalene	Expected Result
PARAFFIN	61.5	43.9	51.3
MONOCYCLO- PARAFFIN	18.5	18.0	15.4
DICYCLO- PARAFFIN	3.1	0.0	2.6
ALKYLBENZENE	14.8	11.4	12.3
INDANE/ TETRALIN	2.0	2.2	1.7
NAPHTHALENE	0.0	24.5	16.7
AVERAGE CARBON NUMBER			
AROMATIC	9.06	8.91	9.55
PARAFFIN	9.50	10.58	9.50

illustrates the results of this perturbation of the jet fuel. The drastic increase in the paraffinic average carbon number from 9.50 to 10.58 reflects the effect of the addition of the C₁₂ dimethylnaphthalene. An increase in the aromatic average carbon number was expected since dimethylnaphthalene is a C₁₂ aromatic; however the results actually decreased. This is due in fact to the average aromatic carbon number calculational method which is based solely on ions of the alkylbenzene series. The mass spectra of dimethylnaphthalene contains a small relative abundance of m/z 91, which is an ion of the alkylbenzene series, which explains the decrease in aromatic average carbon number. The saturate volume percent results of the spiked fuel did not agree with changes expected due simply to dilution. This may be attributed to the incorrect average paraffinic carbon number on which the volume percent calculation is now based. It should be noted that the naphthalene volume percent increased to 24.5% for the spiked fuel which was close to the expected 16.7% theoretical value. These results illustrate the significance of the naphthalene content on the hydrocarbon type analysis results, not only on paraffinic carbon numbers, but on volume percent results as well.

Effect of Chromatographic Resolution on Carbon Number Calculations

The evaluations and comparisons above were made under the assumption that the carbon number calculational techniques produced valid average carbon number results. Since chromatographic separation played such an important role in these determinations, especially for the GC/MS/SD techniques, it was desired to determine the effect of increased chromatographic resolution on the average carbon number

results. Table 3.17 shows the effect of chromatographic separation on the average carbon number results for the four calculational techniques and two separate jet fuels, JP-4 2455 and JP-8X 2429. The chromatographic resolution was increased by changing from a 3 meter column to a 30 meter column. Both fuels demonstrated a dependence on chromatographic separation for all carbon number calculational techniques. In all cases the determination of carbon numbers with increased chromatographic separation, with the exception of the aromatic average carbon number for JP-8X using the SIM DIST #2 method, better agreement was obtained between the GC/MS/DS and the GC/MS/HTA results, and between the GC/MS/HTA and ASTM results. Increased chromatographic separation reduced all average carbon numbers for the JP-4 fuel. Increased chromatographic separation decreased all average carbon numbers for the JP-8X fuel with the exception of the paraffinic average carbon number using the SIM DIST #1 method. These results indicate that the average carbon number results are very much dependent upon the degree of chromatographic separation employed, and that increased chromatographic resolution results in more accurate average carbon number determinations.

Summary of Results

An extensive amount of effort was dedicated to characterization of the GC/MS/HTA method. The injection methods were evaluated in terms of component discrimination which resulted in the development of a non-discriminating injection technique. The method was evaluated in terms of sensitivity and precision. Similar sensitivities were determined to

Table 3.17

Comparison of Average Paraffin and Aromatic Carbon Numbers
for JP-4 2455 and JP-8X 2429 Fuels as a Function of Chromatographic
Separation Using Several Calculational Techniques

CHROMATOGRAPHY CONDITIONS	Aromatic Average Carbon Number			Paraffin Average Carbon Number				
	SIM DIST #1 ^a	SIM DIST #2 ^b	GC/MS/HTA	ASTM	SIM DIST #1	SIM DIST #2	GC/MS/HTA	ASTM
	<u>JP 4 2455 FUEL</u>							
3 METER DB5	10.4(.4)	10.9(.2)	9.06(.07)		12.1(.2)	12.0(.3)	9.50(.08)	
30 METER DB5	9.22(.01)	9.58(.01)	9.00(0)	8.69	8.64(.02)	8.68(.04)	8.95(.06)	8.01
	<u>JP 8X 2429 FUEL</u>							
3 METER DB5	12.1	10.7	8.0(.1)		14	11.1	9.01(.01)	
30 METER DB5	12.07(.06)	12.71(.01)	8.19(.01)	8.14	13.07(.05)	11.59(.06)	9.20(.03)	8.91

SIM DIST #1 Area centroid based on paraffin and alkylbenzene ion summation chromatograms.
SIM DIST #2 Area centroid based on saturates and unsaturates ion summation chromatograms.
Note: Numbers in parenthesis indicate standard deviations.

those calculated in the ASTM technique. The precision was dependent on hydrocarbon type and volume percent.

To characterize and validate the GC/MS/HTA method, a series of experiments were performed. Comparisons of GC/MS/HTA results with the ASTM results were inconsistent and followed no trends. Evaluations of GC/MS/HTA results of synthetic mixtures showed good agreement in some cases but were still inconsistent. The analysis of simple mixtures seemed to validate the Teeter Rule, although excellent agreement was often present. The perturbation fuel analysis introduced a new method for the characterization of HTA methods. The results obtained here were consistent with the expected results and represented a significant contribution towards validation of the method.

A new method for carbon number determination was developed based on GC/MS/simulated distillation. A critical evaluation of this method, the GC/MS/HTA method, and the ASTM method was performed. The results indicated that the GC/MS/HTA and ASTM method underestimate the average carbon numbers which have a significant effect on the volume percent results of HTA methods. Chromatographic resolution affected the GC/MS/SD determination of average carbon numbers. The results indicated better agreement with mass spectral methods upon increased chromatographic resolution.

Finally, as an intricate part of this project, the developed GC/MS/HTA method was documented in the standard ASTM format which was to be utilized by the Pratt and Whitney engineers of the Fuels Division. A duplication of the ASTM standardized GC/MS/HTA method is shown in Appendix D.

CHAPTER IV

PRELIMINARY INVESTIGATIONS OF ALTERNATIVE IONIZATION TECHNIQUES FOR JET FUEL ANALYSIS

The primary goal of this area of study was to investigate alternative ionization techniques in mass spectrometry for the analysis of jet fuels. These studies will cover aspects of both hydrocarbon type analysis and total fuel analysis. The combination of high resolution gas chromatography and alternative ionization techniques such as low-energy electron ionization and methane chemical ionization, will be a powerful tool for the determination of specific components in jet fuels.

Background

Low Energy Electron Ionization

The main effort in the application of low energy electron ionization GC/MS is to evaluate a technique for the specific detection of aromatic type compounds in jet fuels. Studies have been reported (31,53,59) on the determination of specific aromatic components in fuels and coal-derived liquids by such methods. Aromatic compounds have a lower ionization potential than aliphatic molecules which allows for the selective ionization of aromatics in the presence of aliphatics (53).

In the present study the utilization of GC separation, combined with the specific detection of aromatics, is demonstrated as a potential method for the determination of specific aromatic components in jet fuels. A method such as this would contribute to the development of a total fuel analysis method which was previously discussed.

Methane Chemical Ionization

The main effort in the application of methane chemical ionization (CI) GC/MS to the analysis of jet fuels was to demonstrate the potential of the technique as a new method for hydrocarbon type analysis. Much work has been reported on the analysis of fuels and other coal derived liquids using CI/MS (53-58) for the determination of specific fuel components and specific classes of components. With chemical ionization, a large array of specific ionization schemes are available by choosing an appropriate CI reagent gas. Harrison (52) in his book on chemical ionization mass spectrometry, discusses in detail the fundamentals, instrumentation, and applications of CI/MS. In general terms, the ionization specificity in CI/MS is obtained by the specific reactions and energetics encountered by the ionized reagent compound and the analyte. For example, in positive methane CI/MS (which is used in this study), a methane molecule is first ionized to CH_4^+ (and CH_3^+ , CH_2^+ , etc.) by electron impact ionization. Collisions of these ions with another methane molecule leads to proton transfer to form CH_5^+ . This process continues to form higher m/z ions such as C_2H_5^+ . Only those analytes with a higher proton affinity than CH_4 and C_2H_4 (the conjugate bases of CH_5^+ and the C_2H_5^+ ions) will be ionized.

The application of methane CI/MS will be demonstrated as a potential new method of hydrocarbon type analysis of jet fuel. The results are only preliminary and demonstrate the need for continued experimentation. An additional potential for CI/MS is combined gas chromatography CI/MS. This would enable the determination of specific components of specific classes which would contribute to the total fuel analysis effort.

Experimental

All instrumental parameters were unchanged unless otherwise specified in this section.

Electron Energy Variation

The electron energy variation was obtained by manual adjustment of the electron energy control knob. The electron current was maintained at 300 μ A which limited the lowest electron energy to 11.7 eV. The high end of the electron energy was 100 eV.

The sample analyzed was a 50/50 mixture of the Aromatic 150 and Isopar M mixtures. Analysis of the sample at each electron energy was performed separately after adjustment to the proper energy.

Methane CI

Methane CI was performed at an electron energy of 100 eV and a methane source pressure between 0.2 and 0.3 Torr. The mass spectrometer was scanned from 65 to 650 amu with a total scan time of 1.0 s. The samples were analyzed by separate injections of pure components diluted in hexane.

Results and Discussion

The experimental results which follow represent preliminary investigations on the use of alternative ionization MS techniques as specific detectors for hydrocarbon types in jet fuels. The development of a complete method based on these techniques was not the objective these investigations.

Low Energy Electron Ionization

By varying the electron energy in the ion source of the mass spectrometer, the specific detection of aromatic components was obtained in the presence of paraffin components. This is illustrated in Figure 4.1 in which only a select group of aromatic compounds show response. The low energy EI analysis suffers from low sensitivities, as reflected by the total area of each chromatogram, but the selectivity is greatly enhanced. Table 4.1 shows the variation in the combined saturate and unsaturate hydrocarbon type analysis results of this 50/50 aromatic/paraffinic mixture as a function of electron energy. The results illustrate the selective ionization of aromatics (unsaturates) at lower electron energies. To further illustrate the increased selectivity of this ionization method, the mass spectrum of a single chromatographic peak is shown as a function of electron energy in Figure 4.2. The lowest electron energy (11.7 eV) was very selective for the C₄-benzene (possibly butylbenzene), but the response was quite low. In this example only the M⁺ ion was produced. As the energy was increased (13.0 eV) other aromatic mass spectral peaks appeared such as m/z 148 which is indicative of a C₅-benzene M⁺ ion. At 50.1 eV a series of paraffinic peaks appeared which clearly indicated the

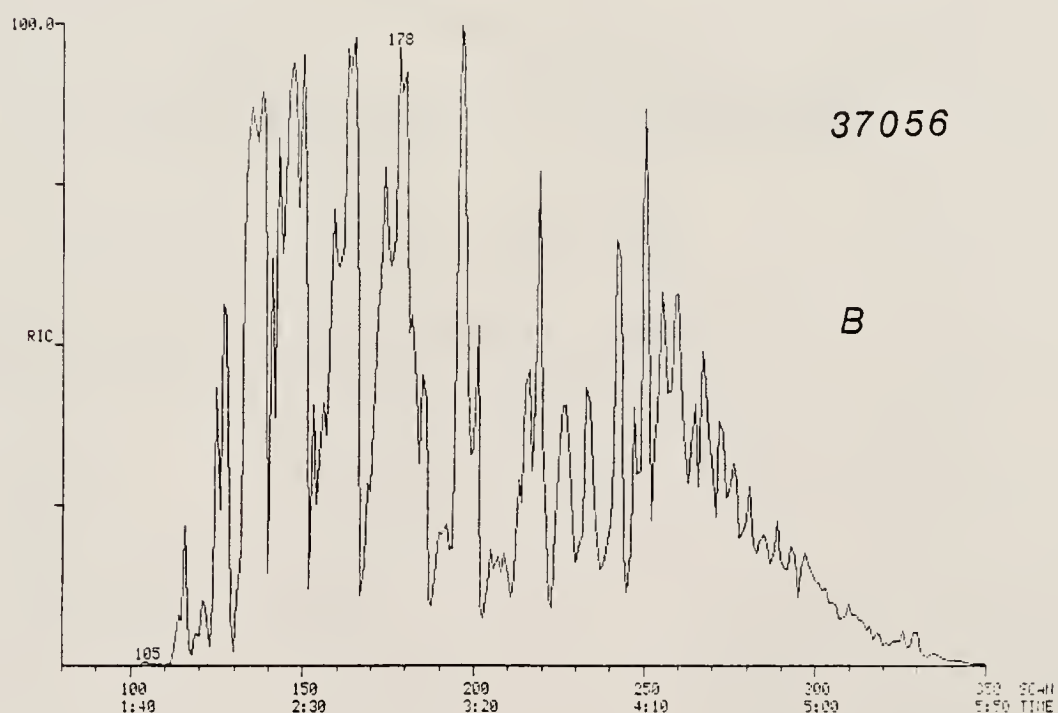
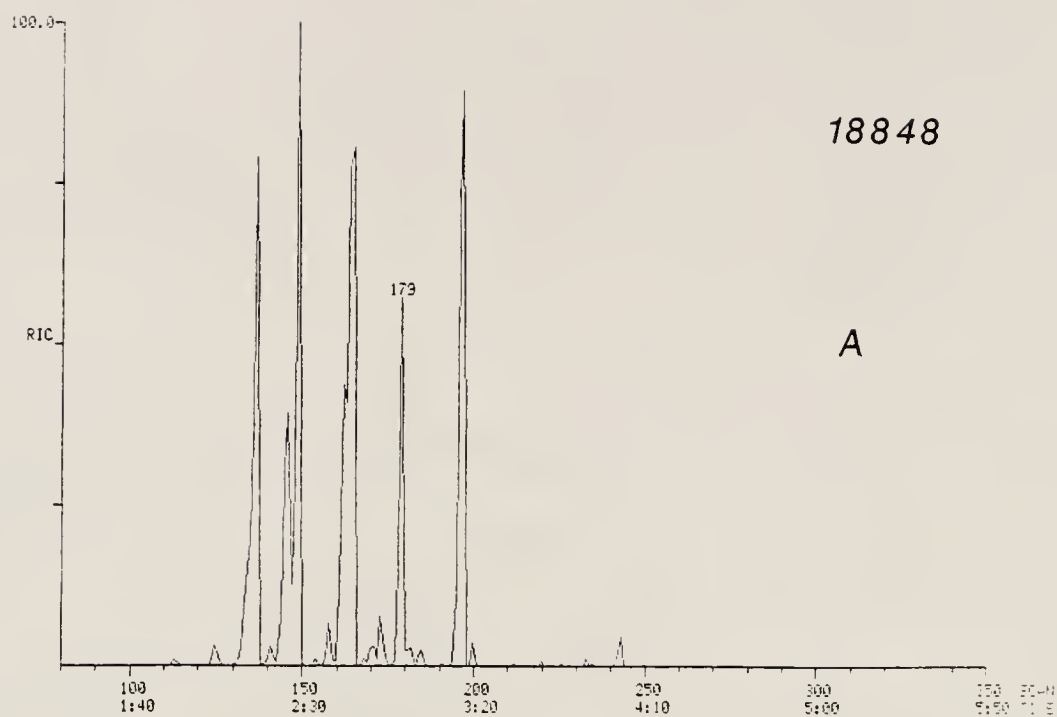


Figure 4.1 The reconstructed ion current chromatograms for a 50/50 paraffin and aromatic mixture at two different electron ionization energies, A) 13.0 eV, B) 50.1 eV.

Table 4.1

Results of Combined Saturates and Combined Unsaturates GC/MS/HTA
of a 50/50 Aromatic 150/Isopar M Mixture
as a Function of Electron Energy
in Volume %

Electron Energy (eV)	Saturates (paraffins)	Unsaturates (aromatics)
11.7	0	100.0
13.0	0.2	99.2
20.0	37.6	62.4
31.0	49.9	51.1
50.1	50.6	49.4
100.0	44.2	55.8

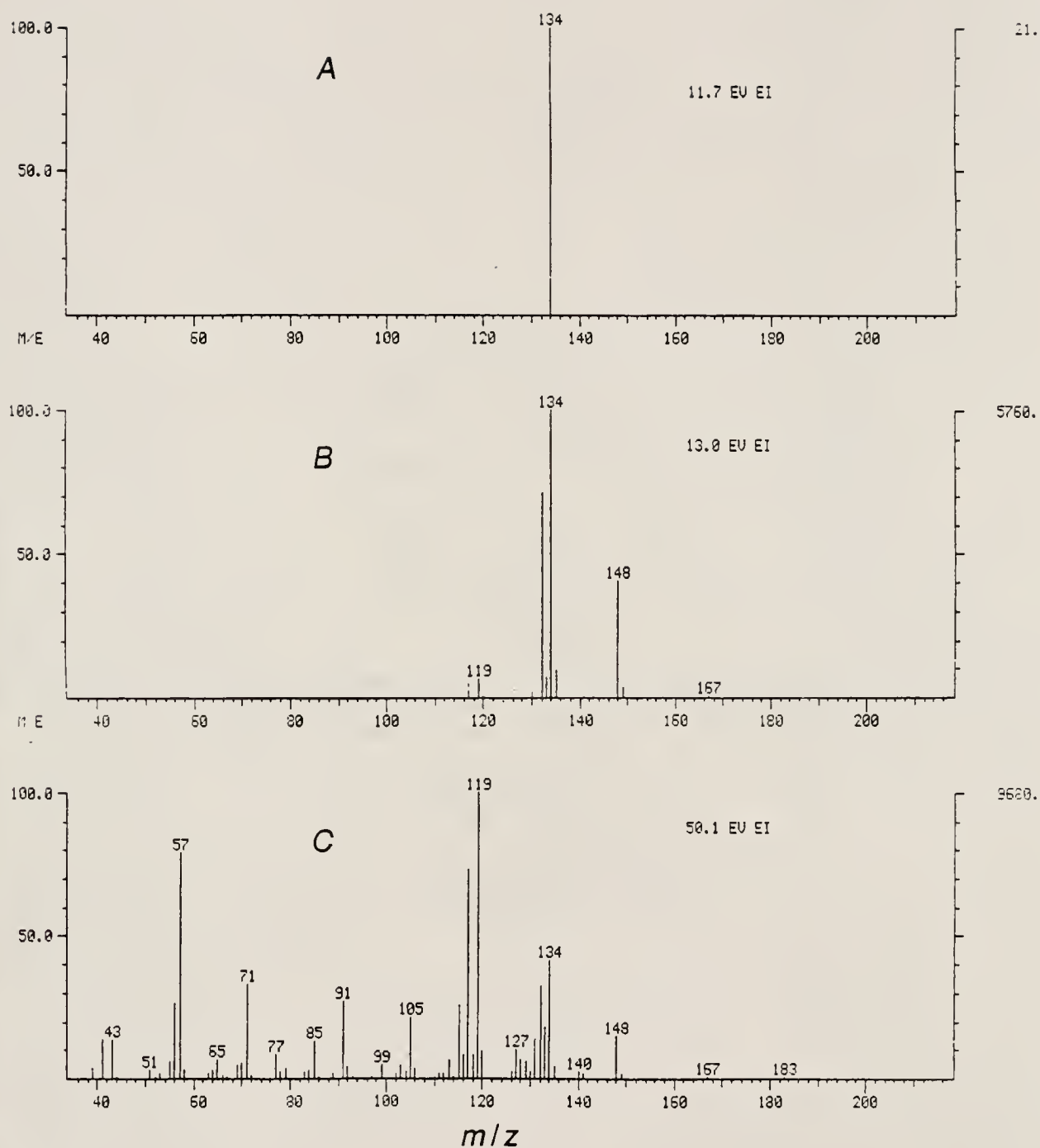


Figure 4.2. The mass spectra of the peaks marked by scan number 179 and 178 in Fig. 4 above at different electron energies, A) 11.7 eV (chromatogram not shown in Fig. 4), B) 13.0 eV, and C) 50.1 eV.

multicomponent nature of this chromatographic peak and the selectivity provided by low electron energies.

These results were obtained on a 3 m column with minimal chromatographic separation. Application of increased GC separation would surely provide a means of specific component analysis of aromatic types in jet fuels.

Methane Chemical Ionization

The ideal method for hydrocarbon type analysis would be to have available a specific detection system for each hydrocarbon type, thus eliminating the need for matrix normalization. This ideal system would best be performed on one instrumental configuration. The methane chemical ionization mass spectra of common hydrocarbons of jet fuels have demonstrated potential as such a detection system. These results are illustrated in the set of figures below in which example compounds of each hydrocarbon class have been analyzed by methane (positive) CI/MS. In most cases a distinct series of ions was formed for each hydrocarbon type. These distinctions for each hydrocarbon type will be briefly discussed. Figure 4.3 illustrates the mass spectra of three different paraffinic compounds. The common fragment ions are m/z 71, 85, and 99. The relative abundance of each seems dependent upon the degree and position of branching. The other major ions are the $[M-1]^+$, and the $[M-15]^+$ for highly branched molecules such as the 2,2,4,6,6-pentamethylheptane. Figure 4.4 illustrates the mass spectra of three cycloparaffinic compounds. The distinction here is the low relative abundance of any fragment ions, with the exception of $[M-1]^+$ ion (base peak), for both substituted and unsubstituted rings. Figure 4.5

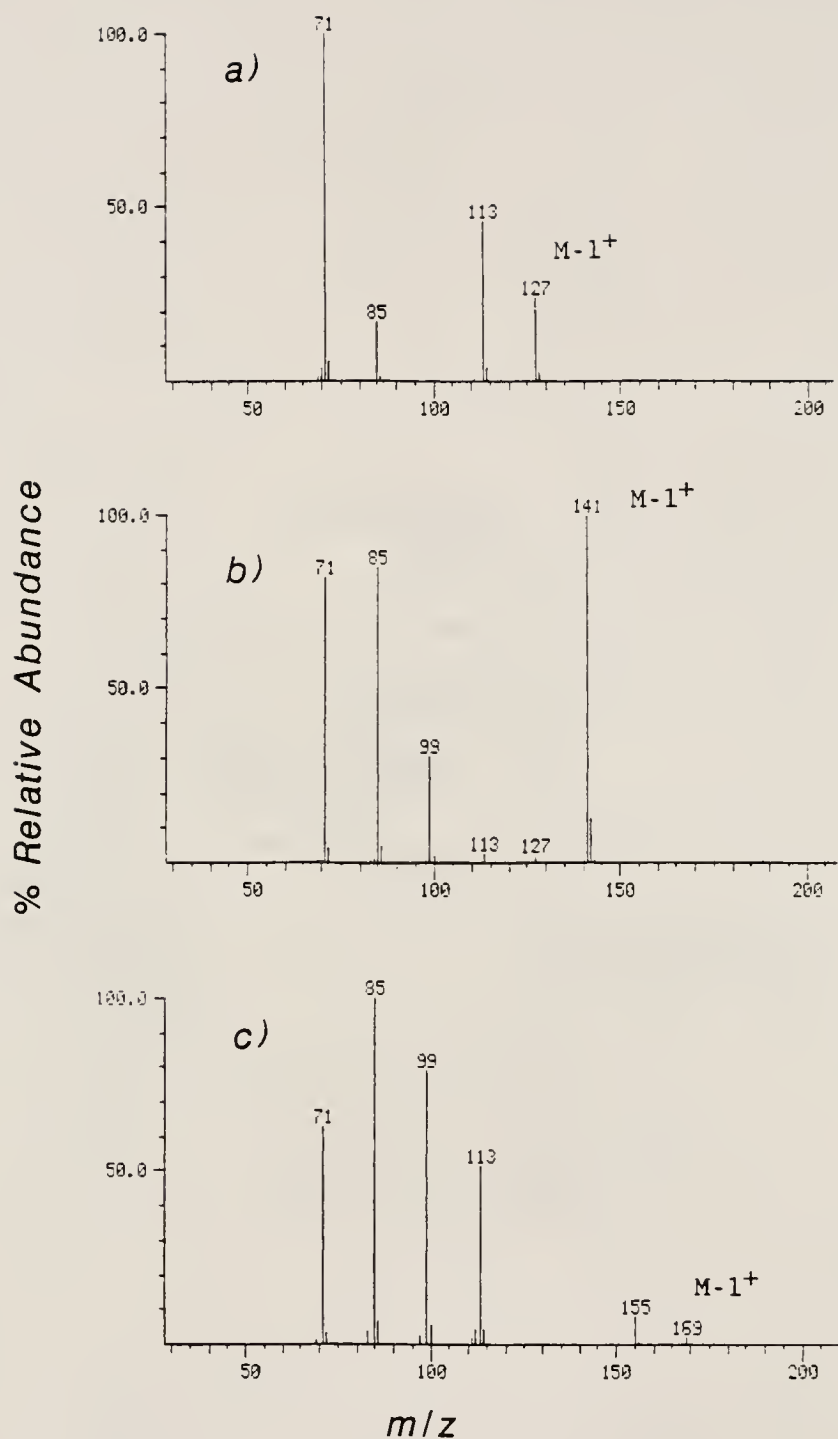


Figure 4.3. Methane chemical ionization mass spectra of a) 2,2,5-trimethylhexane, b) n-decane, c) 2,2,4,6,6-pentamethylheptane.

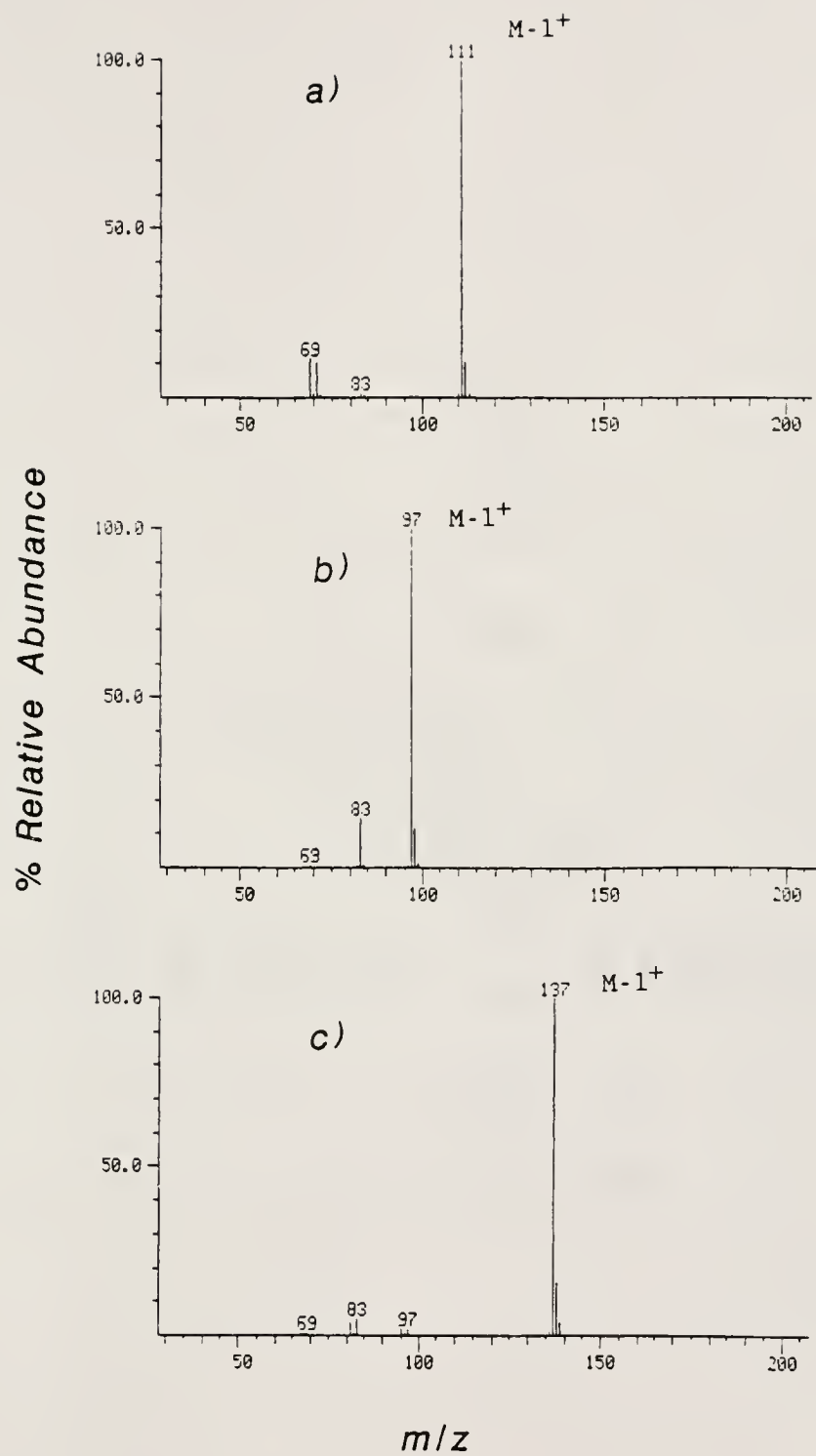


Figure 4.4. Methane chemical ionization mass spectra of a) cyclooctane, b) methylcyclohexane, c) decalin.

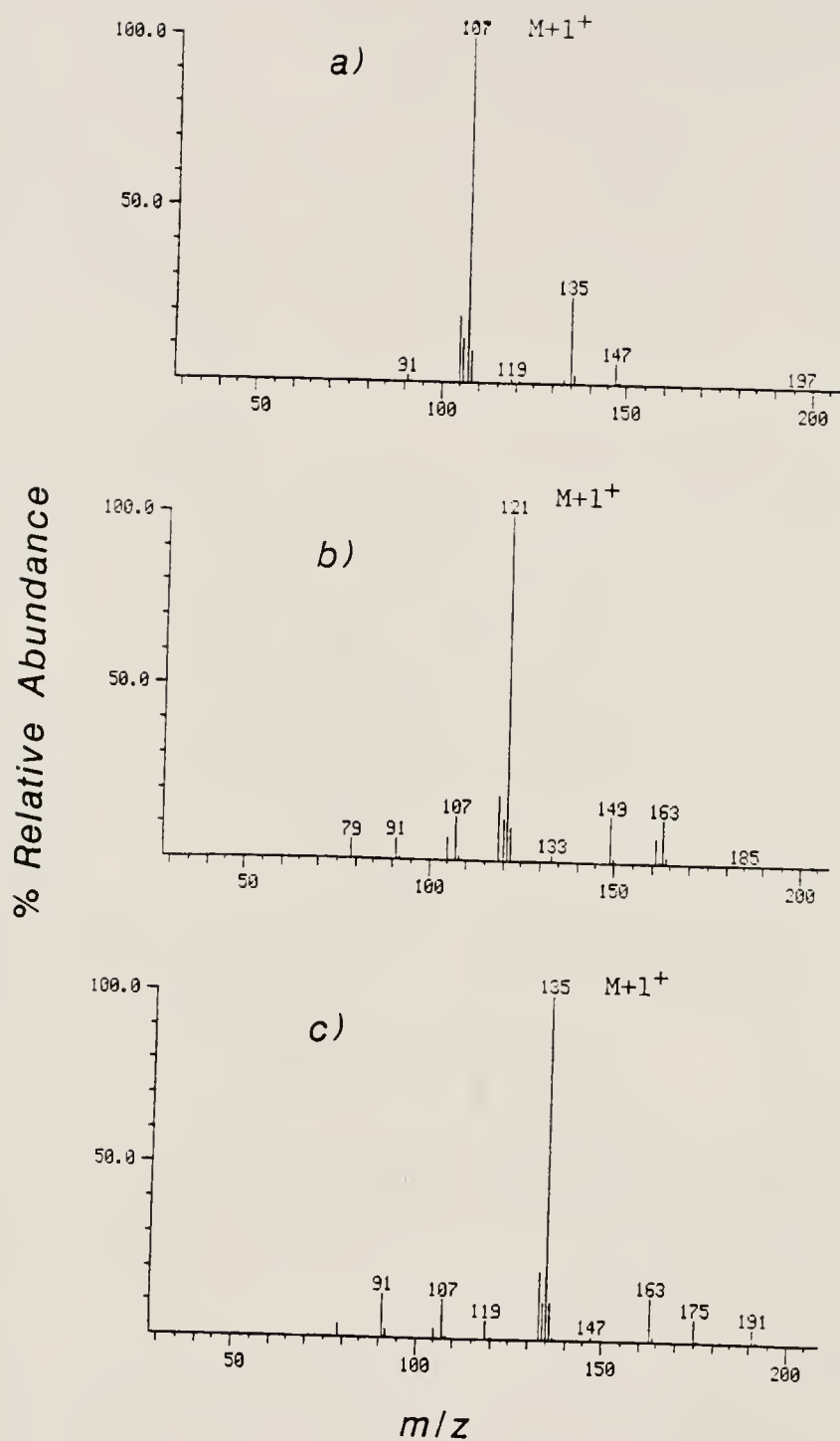


Figure 4.5. Methane chemical ionization of a) p-xylene, b) n-propylbenzene, c) n-butylbenzene.

illustrates the mass spectra of several alkylbenzenes. The distinction here is the formation of the $[M+1]^+$ base peak. Problems arise by the formation of molecular adduct ions such as $[M+29]^+$ and $[M+41]^+$ which are the same mass as the $[M+1]^+$ ions of higher mass alkylbenzenes. However, at least the ions are common within the alkylbenzene type. Figure 4.6 illustrates the mass spectra of indane, tetralin, methyl- and dimethylnaphthalene which also show behavior similar to the alkylbenzenes, except the ions are distinctive for the molecular weights of each of these types. If one were to inspect the mass spectral peaks of all these examples, at 20% or greater relative abundance, there would be no overlap of peaks among the six hydrocarbon types for the examples studied. Such a result is a step towards the development of the ideal detector for hydrocarbon type analysis. This system is by no means complete, since only a few example compounds of each hydrocarbon type have been tested and no real applications have been made towards jet fuel analysis. However, the results do suggest future directions to pursue.

Summary of Results

The above discussion illustrates the utility of alternative ionization techniques for the analysis of mixtures such as jet fuels. Although no results were given for actual jet fuels, several potential methods have been introduced for future work in jet fuel analysis. For the electron energy study, a simple and specific detection scheme for the analysis of the aromatic fraction of fuels was introduced. For the CI/MS study a potentially new hydrocarbon type analysis method was

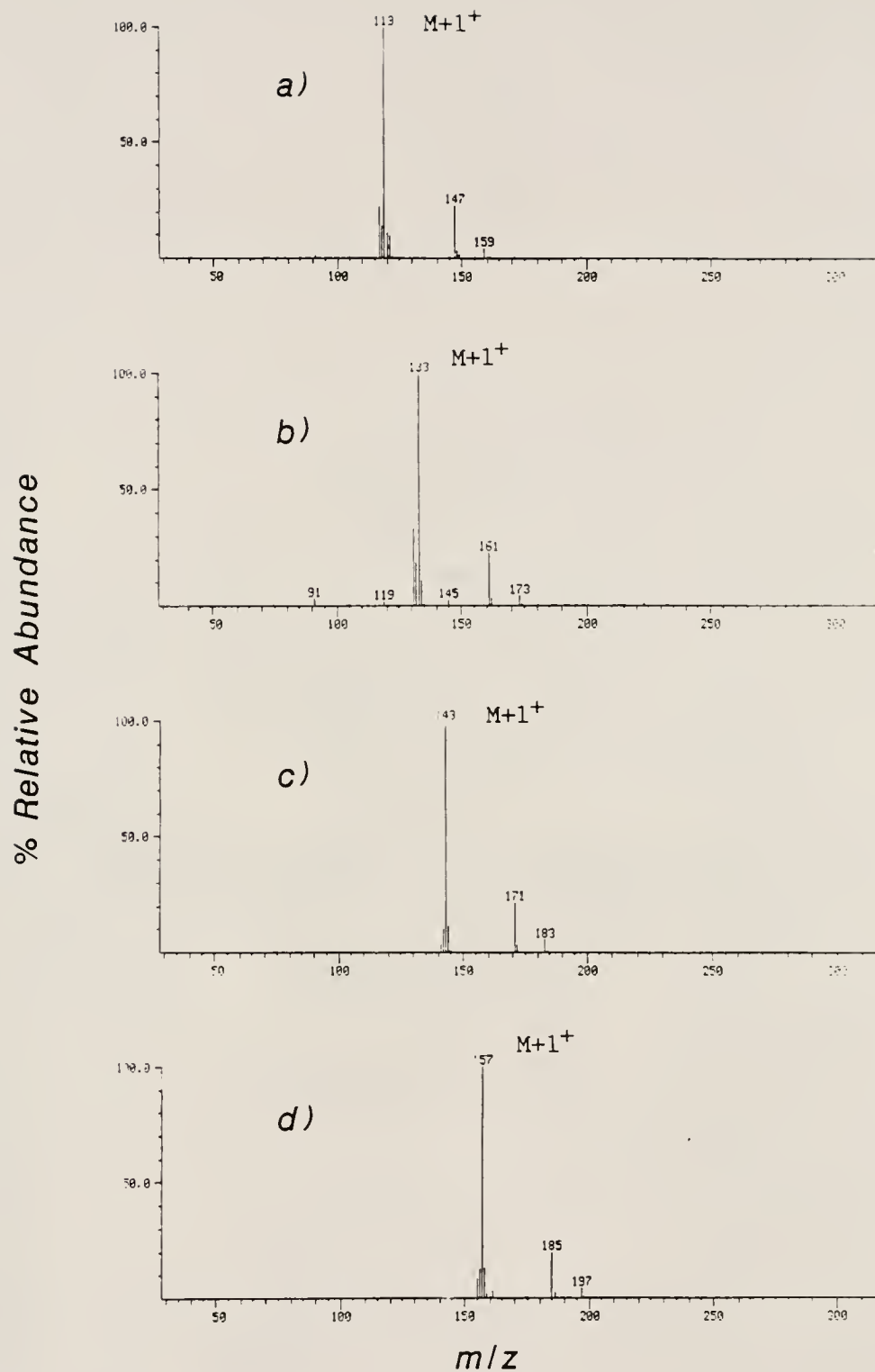


Figure 4.6. Methane chemical ionization mass spectra of a) indane, b) tetralin, c) methylnaphthalene, d) dimethylnaphthalene.

suggested as a result of class specific ions of each hydrocarbon type. This technique be potentially useful not only as an HTA method, but also for specific component analysis when combined with GC separation.

CHAPTER V
PRELIMINARY INVESTIGATIONS OF GC/MS/MS TECHNIQUES
FOR JET FUEL ANALYSIS

The primary goal of this area of study was to investigate GC/MS/MS techniques for the analysis of jet fuels. This chapter will mainly cover aspects of hydrocarbon type analysis, although the major effort was directed toward total fuel analysis. The combination of high resolution gas chromatography and tandem mass spectrometry will be a powerful approach for the determination of specific components in jet fuels.

Background

Mass Spectrometry/Mass Spectrometry

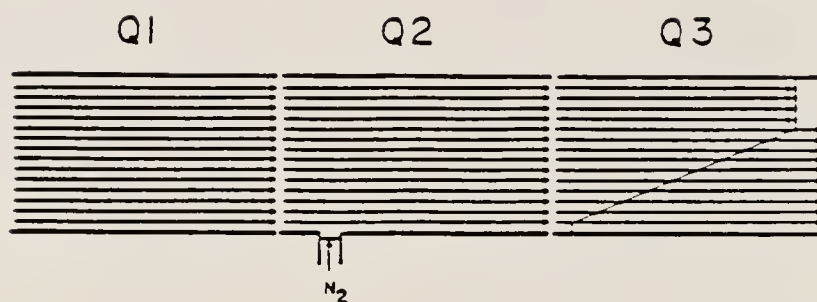
In these studies tandem quadrupole mass spectrometry (TQMS) was used for the evaluation of jet fuel detection schemes. The application of TQMS for the analysis of complex mixtures was first introduced by Yost and Enke (74). The ability to achieve low limits of detection is greatly enhanced over conventional MS systems because of the increased selectivity of MS/MS. McLafferty's book on tandem mass spectrometry (80), has several reviews which deal with the fundamentals, instrumentation, advantages and disadvantages, and applications of MS/MS. The tandem mass spectrometer may operate under several modes

depending on the application. These operational or scan modes are shown in Figure 5.1. Normal mass spectrometry may be obtained by scanning quadrupole one (Q1) or quadrupole three (Q3). The center quadrupole (Q2) is pressurized with an inert gas for collision induced dissociation (CID) reactions. A daughter scan mass spectrum is obtained by selecting a particular m/z (parent ion) with Q1. This ion is fragmented in Q2 by the CID process. The resulting daughter ions are mass-analyzed by Q3, which results in a daughter mass spectrum of the chosen parent ion. This technique is mainly used for structure elucidation and validation of unknown components. A knowledge of the ions observed in the daughter scan mass spectra from a sample is helpful when using the parent scan MS/MS operational mode. A parent scan mass spectrum is obtained by scanning Q1 to sequentially pass all ions produced in the ion source. These ions are fragmented in Q2 by the CID process as Q3 passes an ion of a certain mass (daughter ion). The resulting parent mass spectrum illustrates those parent ions which produce the particular daughter ion by CID. Parent scan mass spectra are quite useful as a screening technique for a particular class of compounds since components within a class of compounds may undergo CID to generate the same daughter ions.

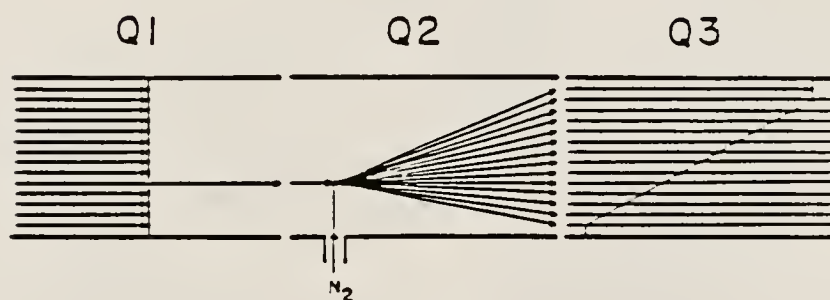
Application of GC/MS/MS to Jet Fuel Analysis

Many applications of MS/MS to fuel analysis have appeared in the literature, as discussed in Chapter I. These application have dealt mainly with the determination of specific components, or a few components of similar classes.

Q3 FULL SCAN MODE



DAUGHTER SCAN MODE



PARENT SCAN MODE

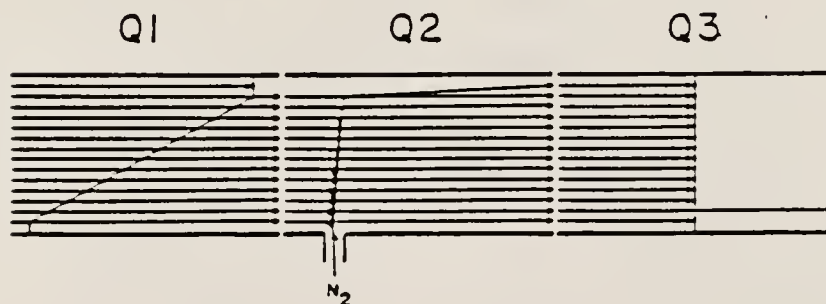


Figure 5.1. Some scan modes of the triple quadrupole mass spectrometer.

The application of combined GC/MS/MS techniques for hydrocarbon type analysis of jet fuels is a novel idea which has been investigated in this study. The success of this technique will be dependent on the ability to implement MS/MS scan modes which are specific for given hydrocarbon types. In other words, the system will be useful only if MS/MS can provide a specific detection method for specific hydrocarbon types (which may vary depending on the number of class distinction pursued). The results of these investigations are discussed below.

The major application of GC/MS/MS foreseen for the analysis of jet fuels is the development of methods for total fuel analysis. For example, a certain hydrocarbon type may be evaluated for specific components by retention time if a type-specific MS/MS scan mode is available for that hydrocarbon type. Of particular importance would be the analysis of jet fuels for trace components such as heteroatomics and fuel additives.

Experimental

All instrumental parameters were unchanged unless otherwise specified in this section.

All MS/MS experiments were performed with nitrogen collision gas at a pressure between 0.1 and 0.2 mTorr. The collision induced dissociation energy was 25 eV. The collision energies were varied under computer control in the energy-resolved study.

Results and Discussion

The following experimental results are preliminary investigations on the use of GC/MS/MS scan modes as specific detectors for hydrocarbon types in jet fuels. The development of a complete GC/MS/MS method was not the objective of these investigations.

MS/MS for Hydrocarbon Type Analysis

To simplify the investigation of GC/MS/MS/HTA methods, only the paraffins and alkylbenzenes were targeted for study. Parent scan mass spectrometry was used since it is best suited for class (or type) screening which was the goal of this study. For these investigations, Isopar M and Aromatic 150 were used as the paraffin and alkylbenzene mixtures, respectively. The daughter ions used in the parent scan mass spectra were determined from the daughter scan mass spectra obtained from each of these complex mixtures. The paraffin daughter ions were those ions contained in the paraffin summation series ($\Sigma 43$) in Table 2.1. The most intense of these ions were the m/z 43, m/z 57, m/z 71, and m/z 85. Of course the choice of parent ions of these daughter ions may affect the results, but the average daughter ion mass spectra of the entire range of paraffinic molecular ions (m/z 100, 114, 128, ... up to m/z 170) were evaluated. These four ions (m/z 43, 57, 71, and 85) were chosen as the daughter ions used in the paraffin parent scan mass spectra.

Figure 5.2 illustrates the average daughter scan mass spectrum of m/z 134 of Aromatic 150. The remaining parent ions of the alkylbenzene series (m/z 120, m/z 148, and m/z 162) produced similar daughter scan mass spectra. Therefore the four most intense daughter ions (m/z 77,

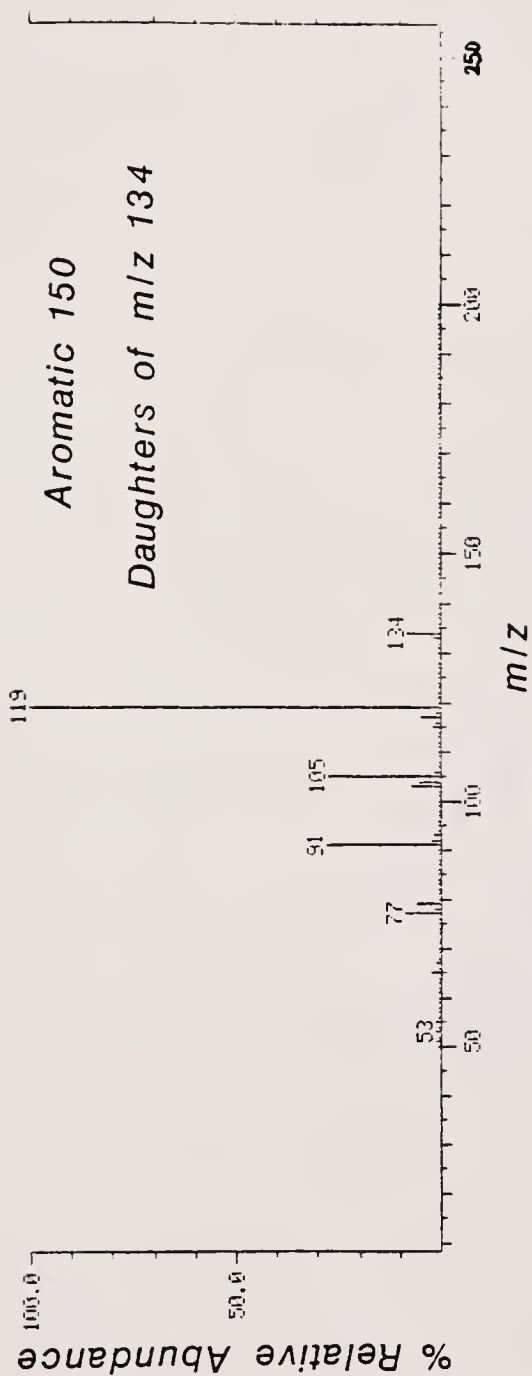


Figure 5.2. Average daughter ion mass spectrum of m/z 134 of Aromatic 150.

m/z 91, m/z 105, and m/z 119) were chosen as the daughter ions used in the alkylbenzene parent scan mass spectra. Figure 5.3 and Figure 5.4 illustrates the selectivity of these two parent scan modes. The parent scans of alkylbenzenes daughter ions respond to Aromatic 150 and not to Isopar M, whereas the parent scans of paraffin daughter ions respond to Isopar M and not to Aromatic 150. This would provide a HTA method if distinction were desired between only these two classes. The Finnigan TSQ45 mass spectrometer is limited by the number of parent scan mass spectra it may acquire under one run. Ultimately parent scans for all six hydrocarbon types would be desired. Therefore, one or two parent scans would have to be chosen for each hydrocarbon type. Because of this, investigations were made into the differences between parent scans of different daughter ions. Figure 5.5 illustrates the Isopar M chromatograms of the four paraffin parent scans. Little difference is observed between the chromatograms for parent ions of m/z 43, m/z 57, and m/z 71, except that the parents of m/z 71 were only 25% of the response of the others. The chromatogram for the parents of m/z 85 shows very little response. Therefore a single parent scan for m/z 43 or m/z 57 might be used for detection of all paraffins since little discrimination is observed for either daughter with respect to retention.

The chromatograms for the parents of the alkylbenzene daughter ions were quite different in comparison. Figure 5.6 illustrates the Aromatic 150 chromatograms from the four alkylbenzene parent scans. There are obviously some distinctions between the four parent scans, as evident by the different chromatographic profiles produced. Clearly,

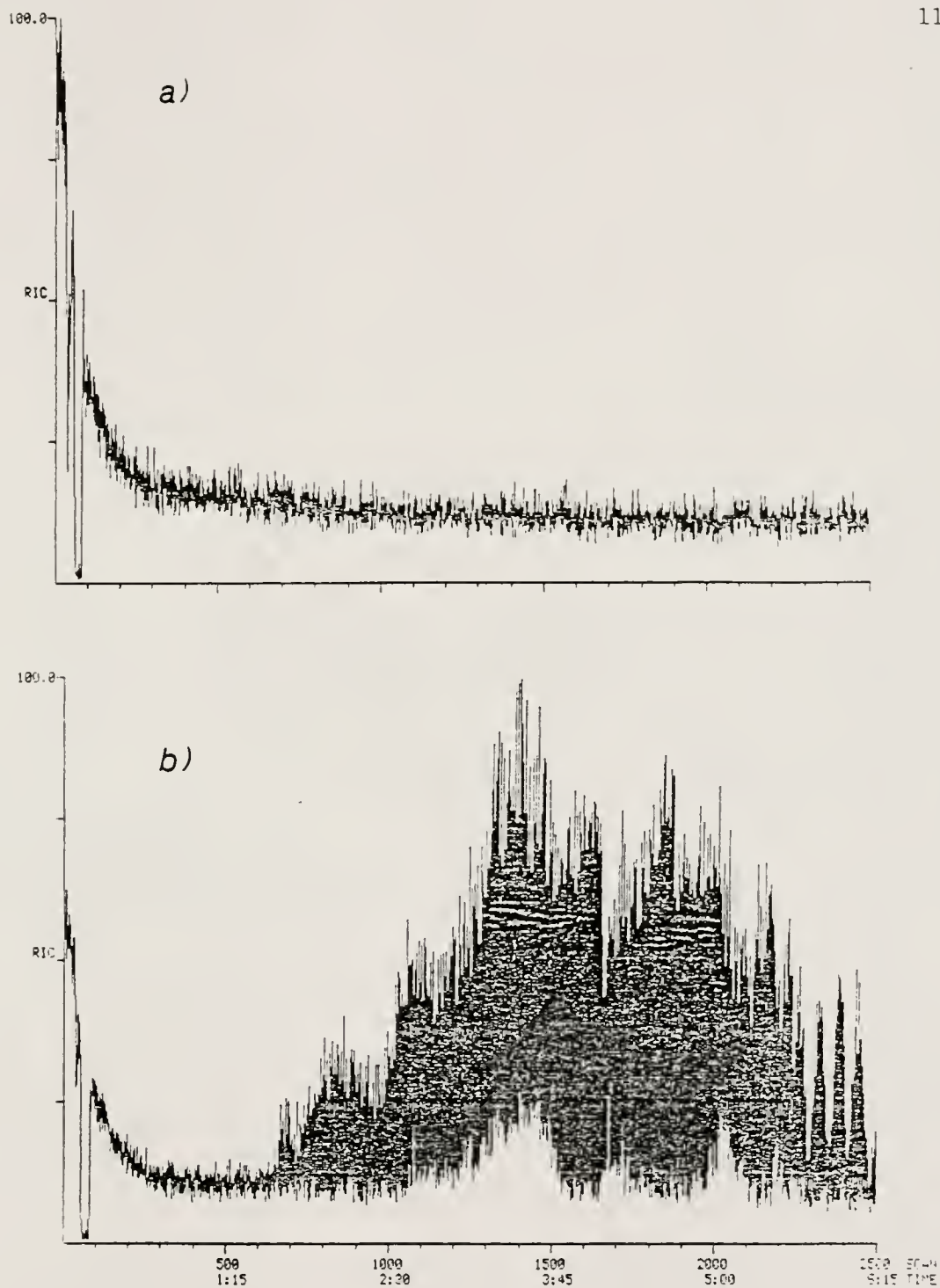


Figure 5.3. The GC/MS/MS (parents of alkylbenzene ions, m/z 77, m/z 91, m/z 105, and m/z 119) reconstructed ion current chromatograms of a) Isopar M and b) aromatic 150.

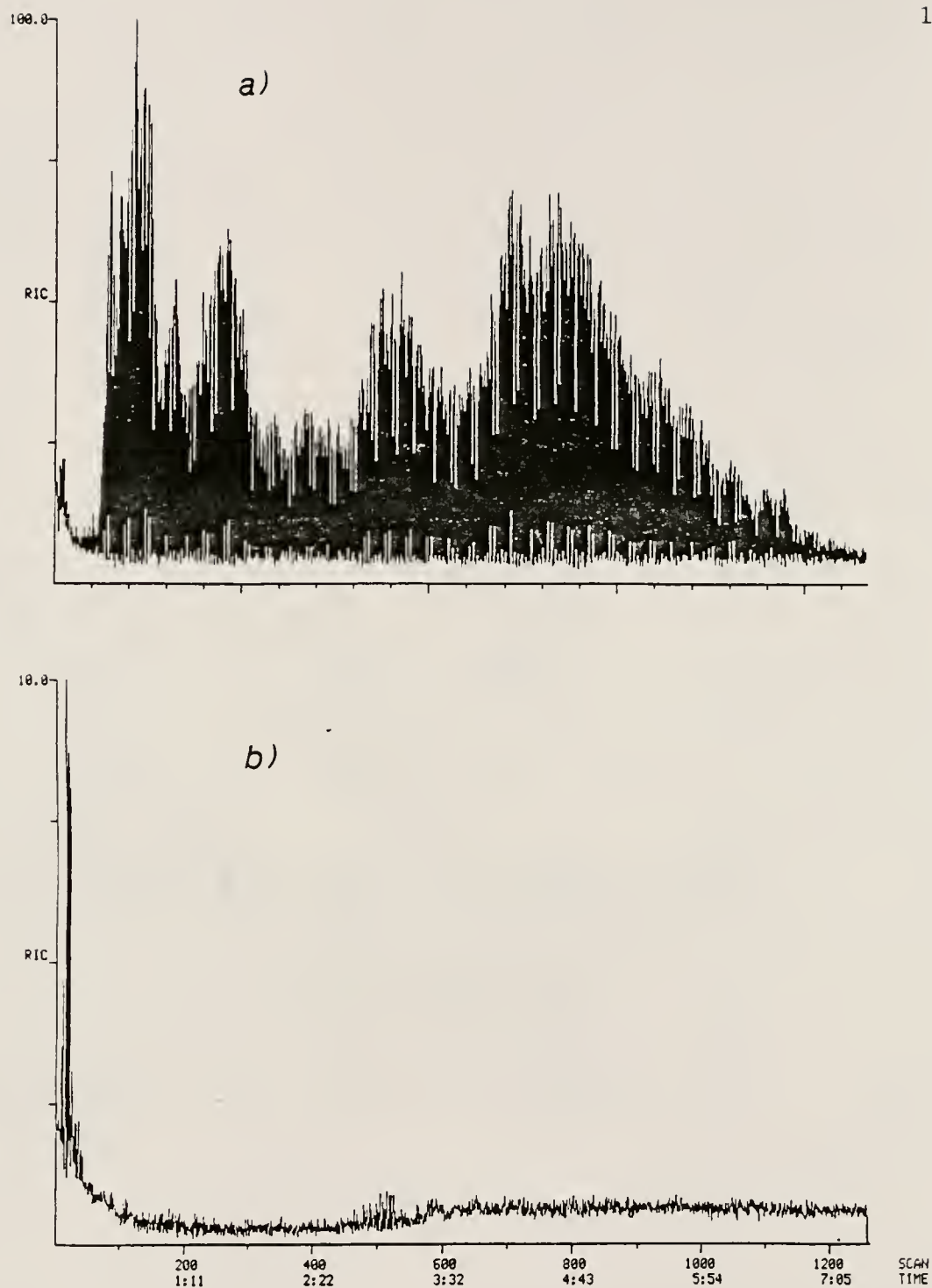


Figure 5.4. The GC/MS/MS (parents of paraffin ions, m/z 43, m/z 57, m/z 71, and m/z 85) reconstructed ion current chromatograms of a) Isopar M and b) Aromatic 150 (enlarged X10).

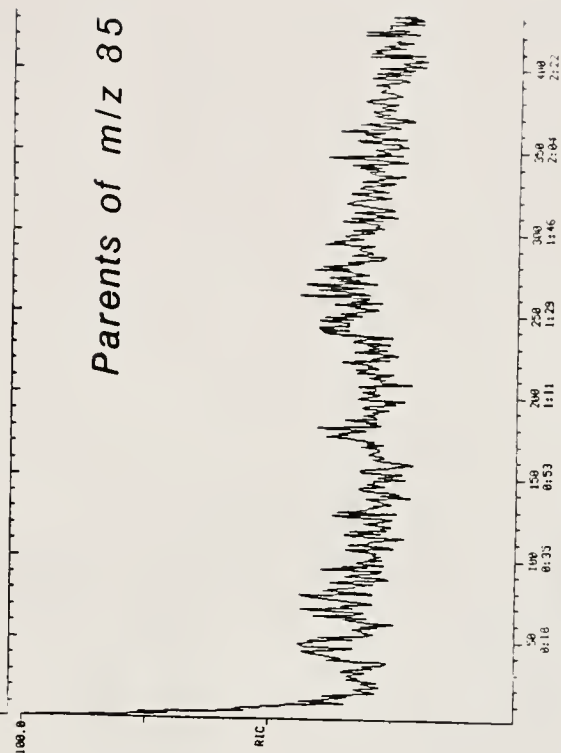
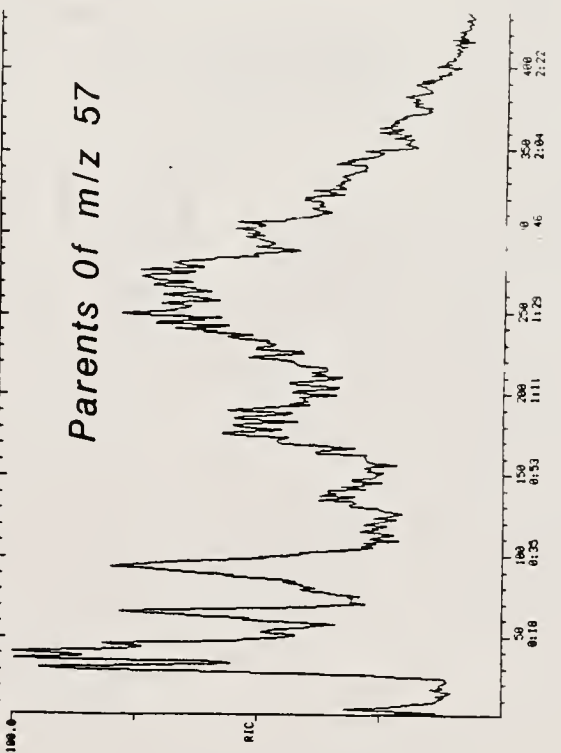
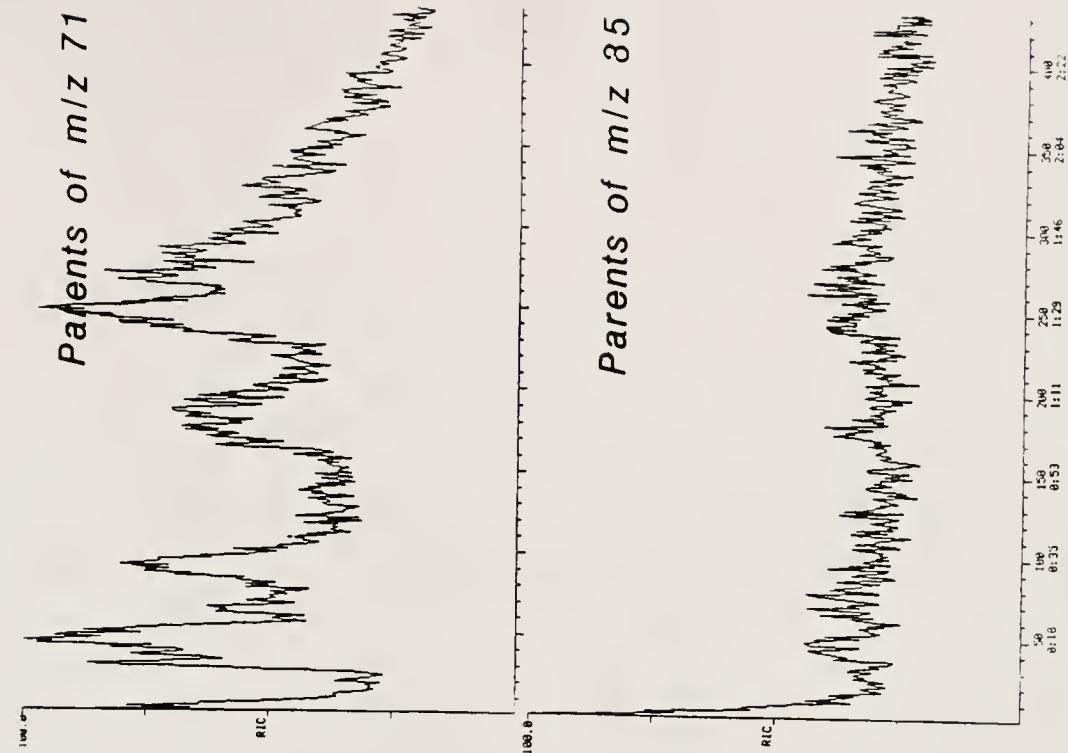
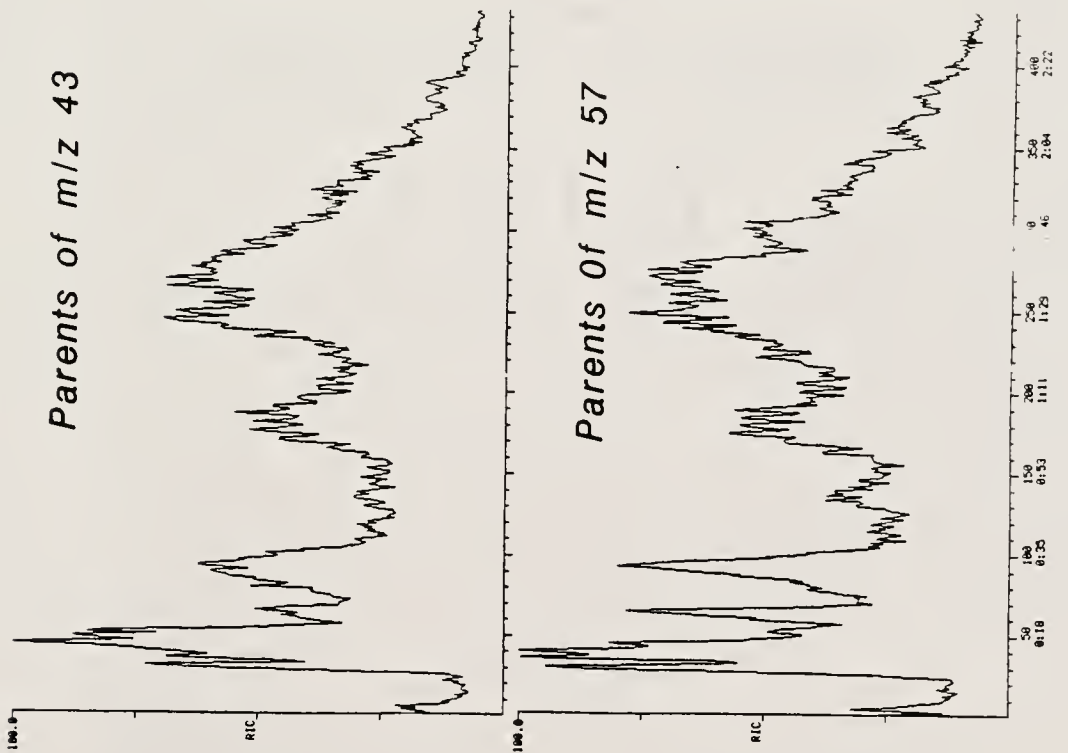


Figure 5 5 The GC/MS/MS (parents of paraffin ions, m/z 43, m/z 57, m/z 71, and m/z 85) reconstructed ion current chromatograms for each individual parent scan for Isopar M.

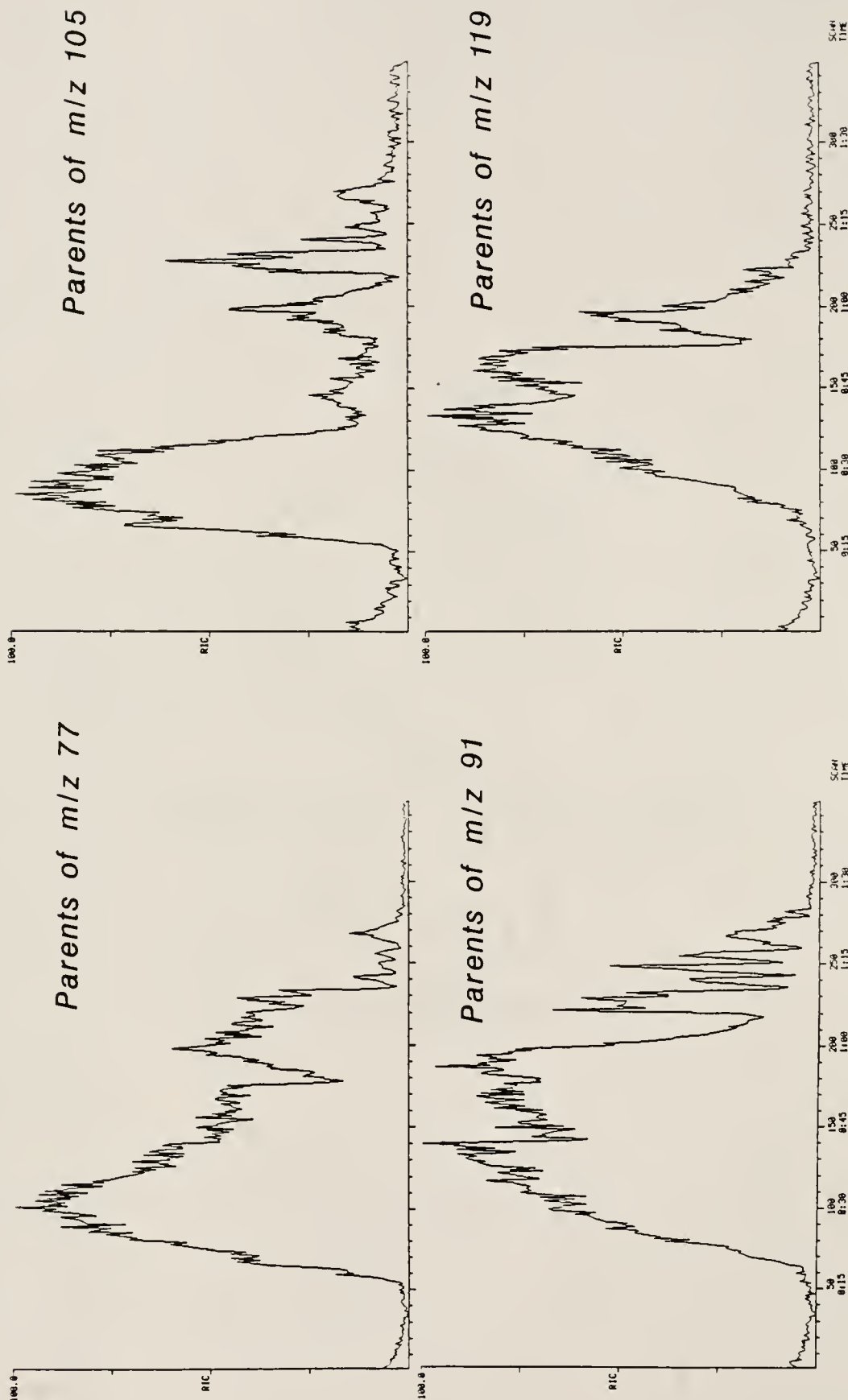


Figure 5.6. The GC/MS/MS (parents of alkylbenzene ions, m/z 77, m/z 91, m/z 105, and m/z 119) reconstructed ion current chromatograms for each individual parent scan for Aromatic 150.

alkylbenzenes of higher molecular weight (longer retention times) fragment upon CID to form different daughter ions. Therefore it is not possible to choose one particular parent scan to represent the alkylbenzenes as a whole.

It would be quite useful to perform the parent scan analysis of all hydrocarbon types for each characteristic daughter ion, but as mentioned above, the method would be limited due to the sampling time required by the mass spectrometer to scan over the various daughter ions. A preliminary investigation was made into the application of parent scan GC/MS/MS for HTA of a jet fuel (JP-7) to provide an example of how the method could be applied. Figure 5.7 illustrates the results of this experiment, in which one parent scan was performed for each of the six hydrocarbon types (parents of paraffins, m/z 57; parents of monocycloparaffins, m/z 69; parents of dicycloparaffins, m/z 81; parents of alkylbenzenes, m/z 119; parents of indanes and tetralins, m/z 117; and parents of naphthalenes, m/z 128. The corresponding HTA results were: paraffins, 50%, dicycloparaffins, 17%; alkylbenzenes, 20%; and indanes and tetralins, 1%. The maximum intensities in the parent scan chromatograms correlate with the HTA results quite well except for the alkylbenzene parent scan for m/z 119 which would not be expected to detect all alkylbenzenes as discussed above.

Other GC/MS/MS Modes of Analysis

As mentioned above, the greatest potential for GC/MS/MS analysis of jet fuels involves the determination of specific components or specific classes of components. The tandem mass spectrometer has the ability to profile the molecular weight parent ion distribution of a daughter ion

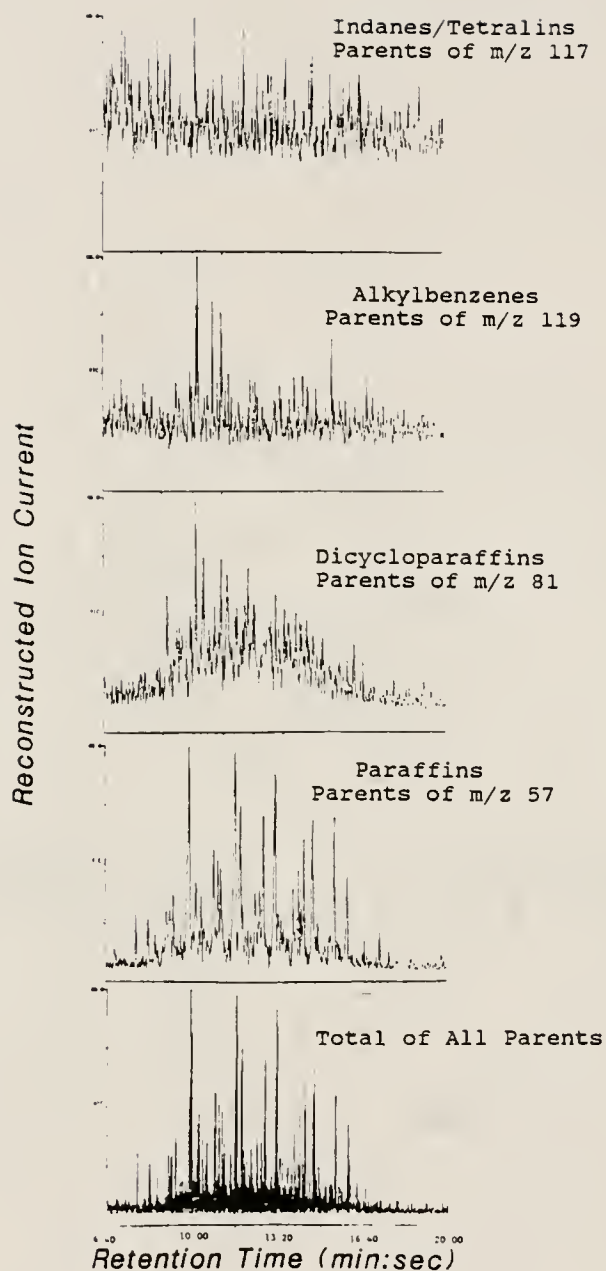


Figure 5.7. The MS/MS reconstructed ion current chromatogram of a select set of 4 parent scans (hydrocarbon types) for JP-7 jet fuel.

from a specific class of compounds. Figure 5.8 shows the results of a parent scan of m/z 105 for Aromatic 150. A profile of each parent ion is displayed which corresponds to the particular parent/daughter ion pair. The distribution of molecular weights of the alkylbenzenes may be visualized from this display. Furthermore, quantitation may be obtained for each particular parent/daughter pair. One might assume that the same information could be obtained using mass chromatograms obtained by normal GC/MS. Figure 5.9 shows the same Aromatic 150 mixture analyzed by normal mass spectrometry and the results displayed as mass chromatograms. It is quite evident that GC/MS does not provide the distinct molecular weight distribution obtained with the GC/MS/MS.

Differentiation of Isomeric Hydrocarbon Types

As discussed previously in Chapter III, there is a need to differentiate between cycloalkane and olefin hydrocarbon types in jet fuels. In the HTA methods, no differentiation is made between the two isomers in the final volume percent results. As shown in Chapter III, erroneous behavior may result where large concentrations of olefins are present. Therefore, the ability to assess the olefin concentration separate from the cycloalkane concentration would be very beneficial in the hydrocarbon type analysis of fuels.

The ability to differentiate between isomeric cycloparaffins and olefins of the same carbon number by normal EI/MS has already been presented in Figure 3.14-3.16. However, not all isomers of the same carbon number produce such different EI mass spectra. Figure 5.10 illustrates the EI mass spectra obtained for cyclooctane, 1-octene, and ethylcyclohexane, all C8 isomers. Subtle differences in the mass

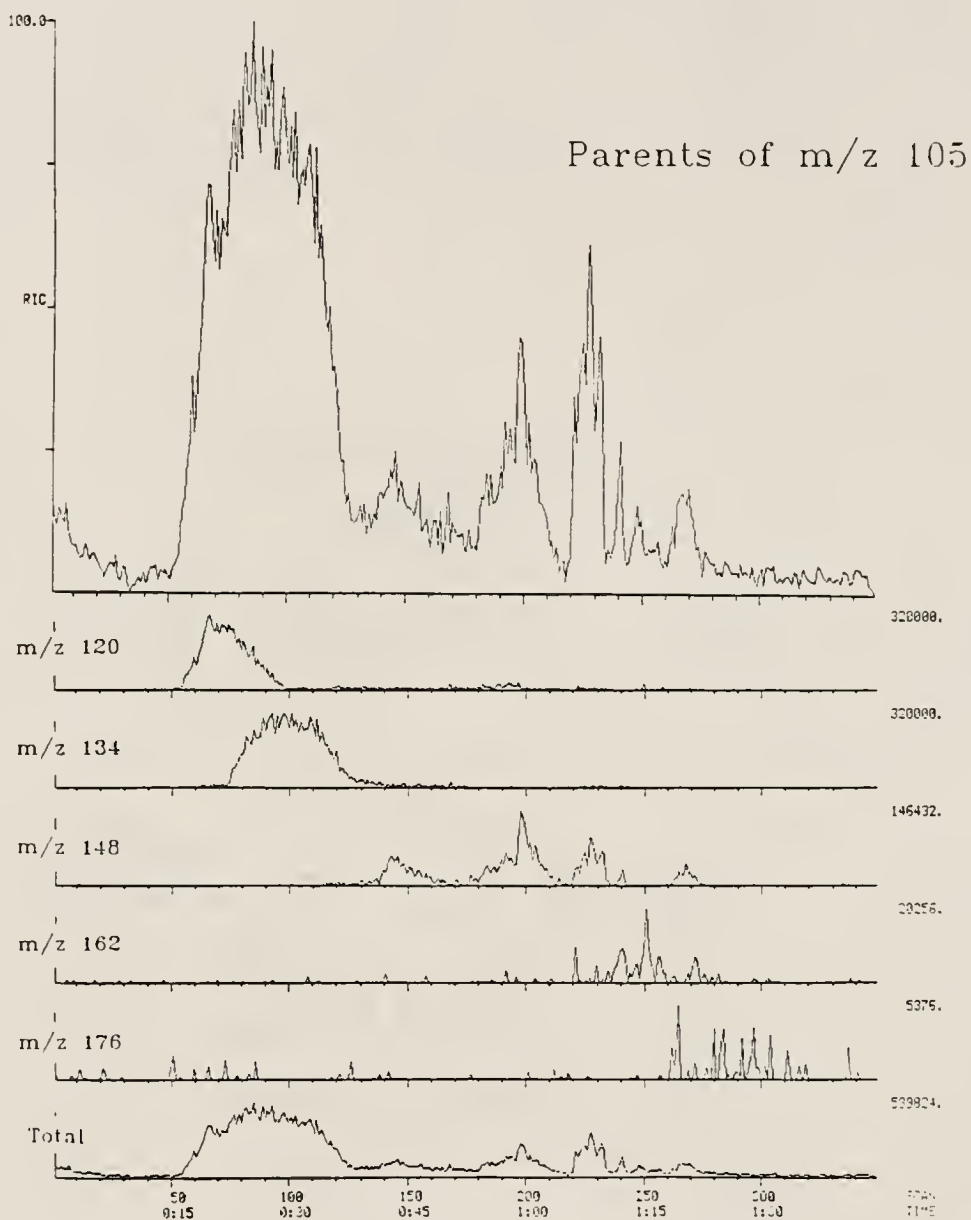


Figure 5.8. The MS/MS (parents of m/z 105) reconstructed ion current chromatogram for Aromatic 150 and the corresponding mass chromatograms of the common alkylbenzene parent masses.

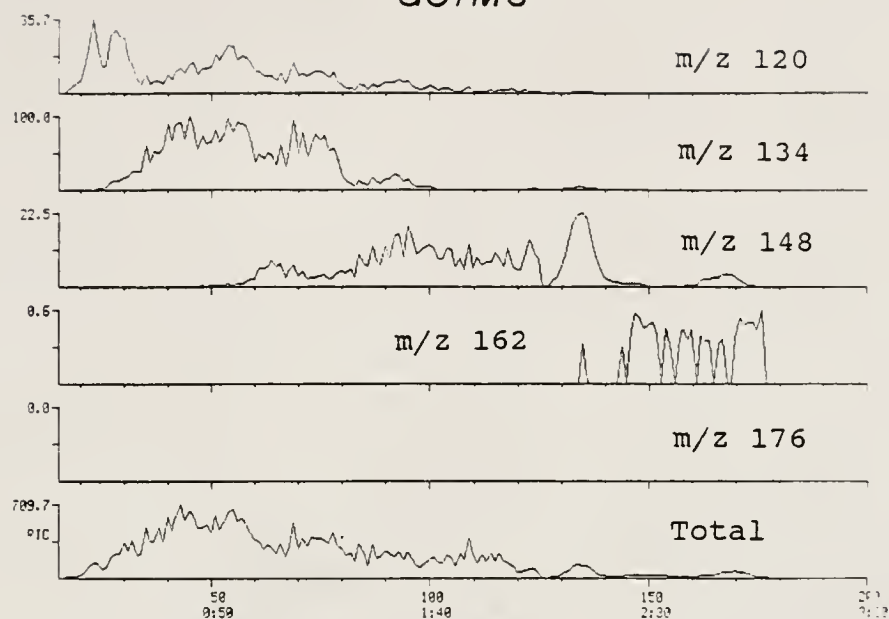
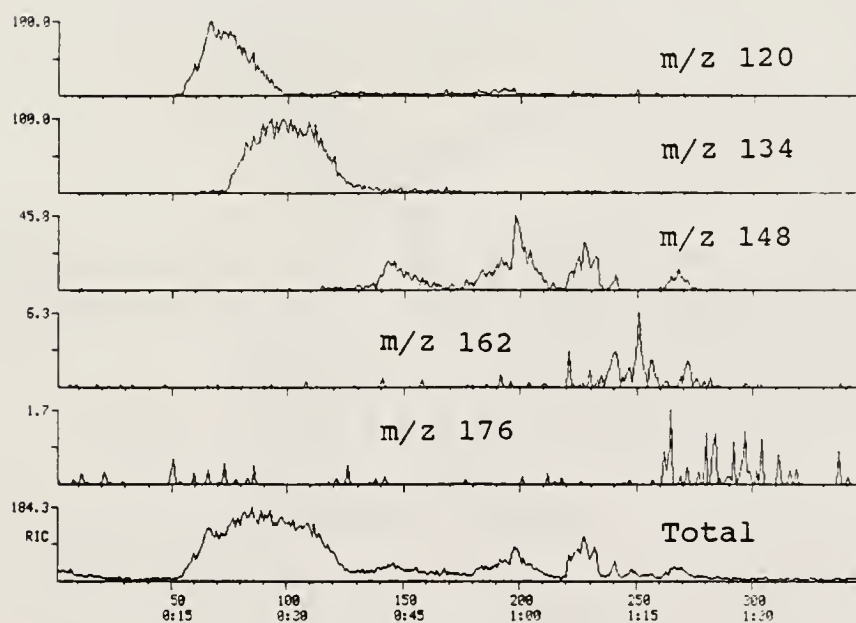
*GC/MS/MS-Parents of m/z 105*

Figure 5.9. Comparison of normal GC/MS mass chromatograms and GC/MS/MS parent scan mass chromatograms for molecular weight distribution.

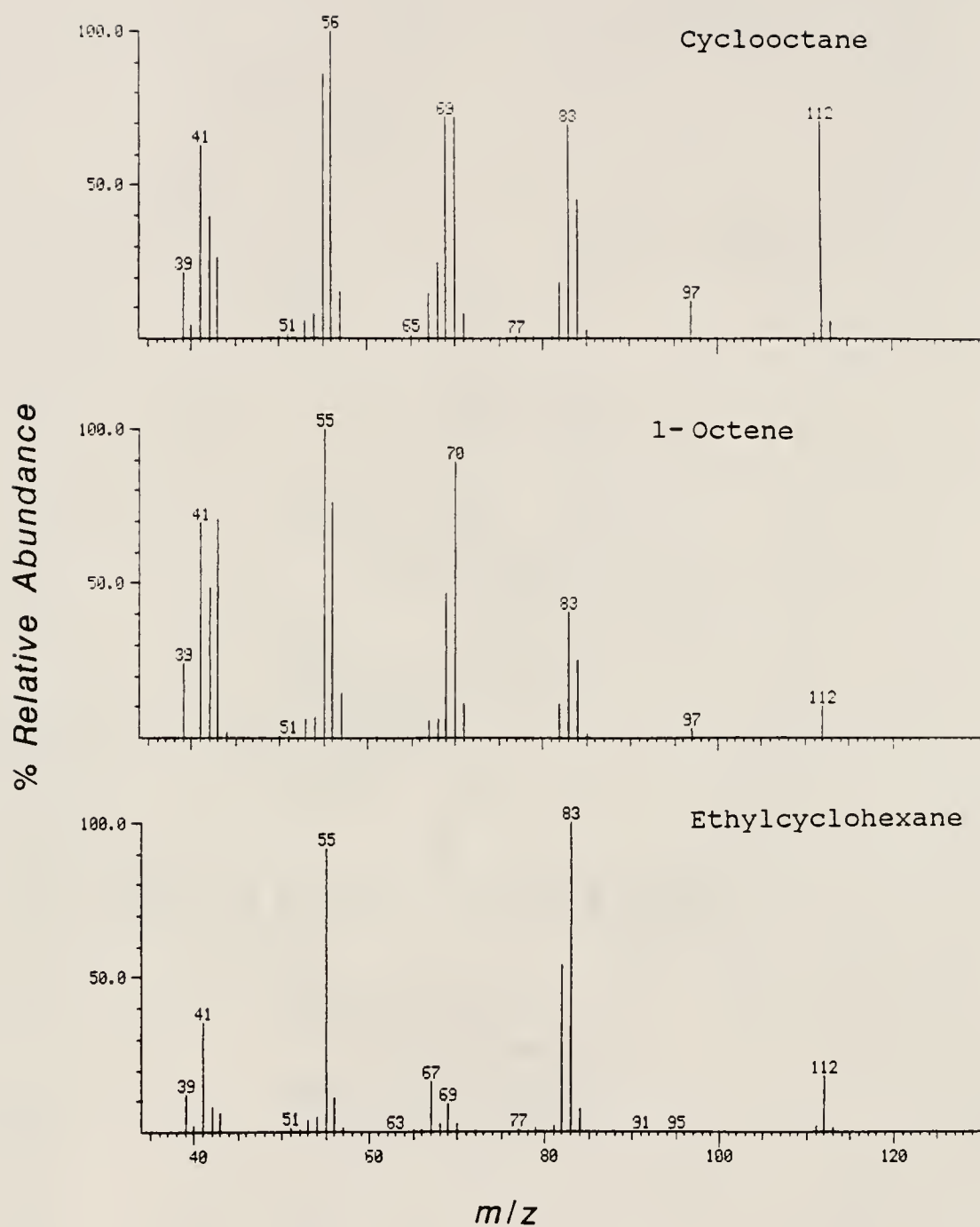


Figure 5.10. The EI mass spectra of cyclooctane, 1-octene, and ethylcyclohexane isomers.

spectra can be seen between the cyclooctane and octene isomers when compared to the significantly different ethylcyclohexane isomer. This demonstrates the need for new GC/MS methods for the differentiation of cycloparaffin and olefin isomers.

The application of MS/MS in the daughter scan mode may provide the capability to distinguish between cycloalkane and olefin isomers. Fetterolf and Yost (81) have demonstrated the ability to differentiate between isomeric ion structures by energy-resolved CID breakdown curves. In such a study the relative abundances of a characteristic set of ions is plotted versus the CID collision energy. Each isomer may produce a distinguishable energy breakdown curve different from the other isomer. Figure 5.11 and Figure 5.12 illustrates the variation in the fragmentation pattern of the daughter ion mass spectra obtained for M^+ ions of cyclooctane and 1-octene, respectively, at two different collision energies. At higher collision energies (25 eV), greater fragmentation has resulted, as indicated by the presence of low mass fragments arising from single bond cleavage and the absence of higher mass fragments. At lower collision energies (5 eV), less fragmentation was observed as indicated by the higher mass fragments arising from rearrangement reactions (even m/z). It is evident from these results that the low energy CID process resulted in a more distinguishable daughter ion mass spectrum. Certainly these results demonstrate the possibility of applying energy-resolved breakdown studies for the differentiation of cycloalkane and olefin isomers. However, the discovery of some characteristic fragmentation ion which distinguishes between cycloparaffin and olefin isomers for all carbon numbers would

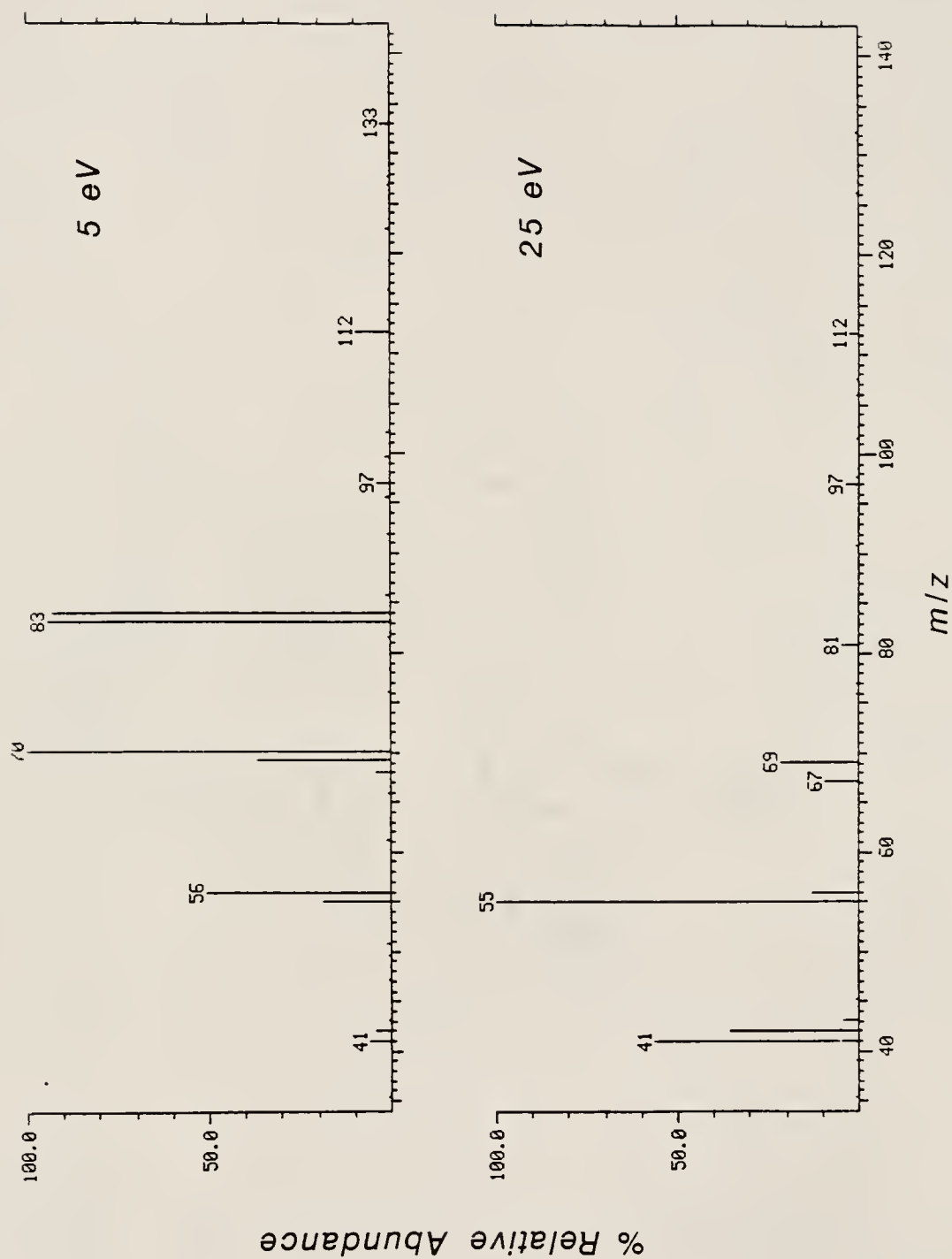


Figure 5.11. The MS/MS daughter ion mass spectra of the M^+ ion (m/z 112) of cyclooctane at two CID collision energies, 5 eV and 25 eV.

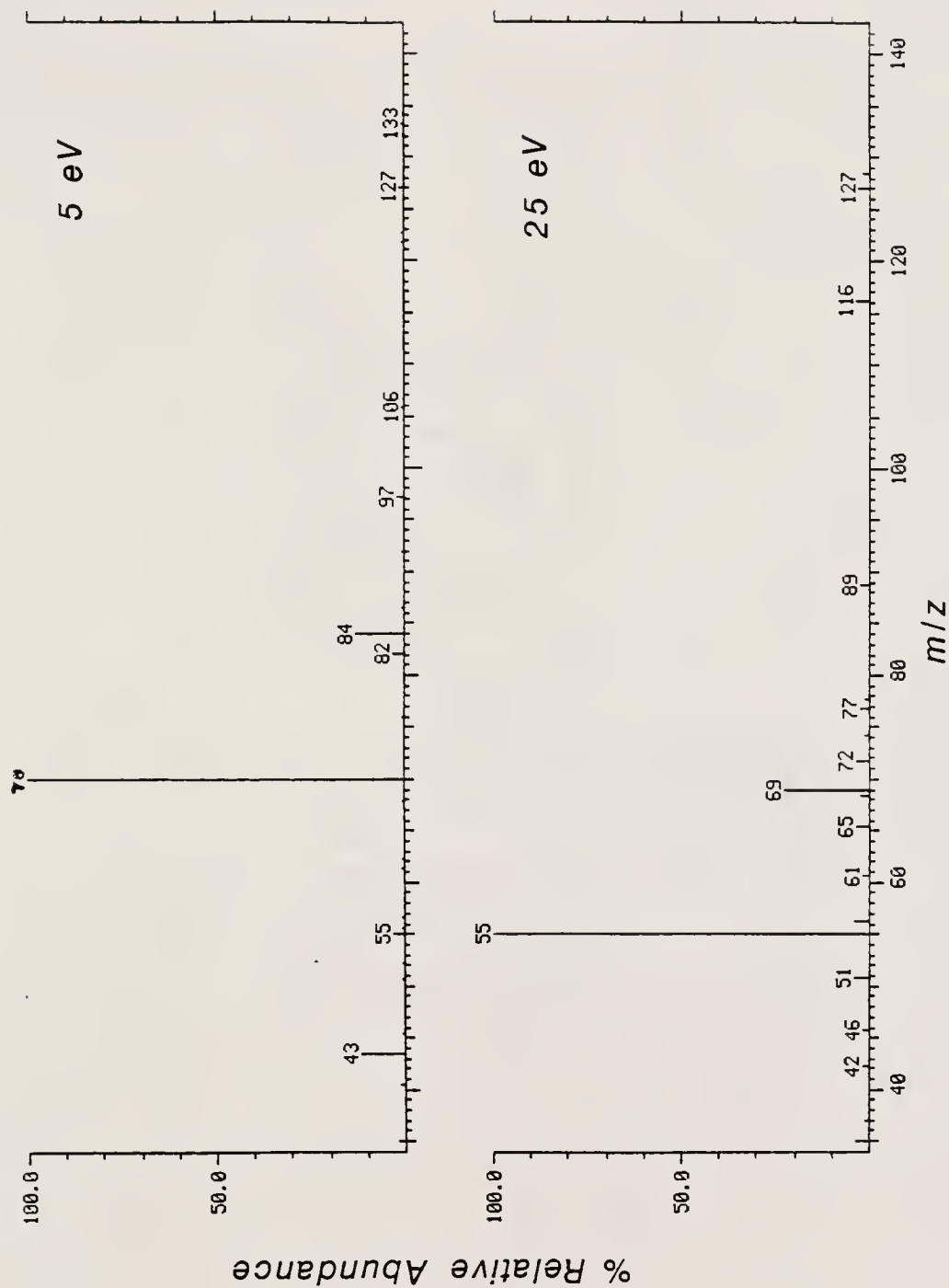


Figure 5.12. The MS/MS daughter ion mass spectra of the M^+ ion (m/z 112) of octene at two CID collision energies, 5 eV and 25 eV.

be much more desirable. The possibilities of such a case are illustrated in Figure 5.13 in which the 5 eV daughter ion mass spectra of the molecular ions of the two isomers are compared. For the cyclooctane isomer, much larger relative abundances were observed for m/z 83 and m/z 84 which correspond to neutral losses of C_2H_3 and C_2H_4 . This neutral loss is greater for the strained cyclic structure than for the linear olefin molecule (81). The behavior of this isomeric pair does not necessarily reflect the behavior of all cycloparaffin/olefin isomeric pairs; however, further investigations may prove quite useful.

Summary of Results

The application of GC/MS/MS to the analysis of jet fuels has been demonstrated to have a significant potential for solving some of the existing problems associated with jet fuel analysis. The differentiation between paraffinic and aromatic mixtures was made using parent scan GC/MS/MS. Differentiation of hydrocarbon types in a jet fuel was demonstrated using a single parent scan for each hydrocarbon type. The relative intensity of the mass chromatograms for each parent scan agreed with the GC/MS/HTA results. The molecular weight distribution may be displayed using mass chromatograms and parent scan MS/MS. Finally, the potential of daughter scan MS/MS as a technique for differentiation between cycloalkane and olefin isomers was demonstrated.



Figure 5.13. Comparison of MS/MS daughter ion mass spectra of the M^+ ions (m/z 112) of cyclooctane and 1-octene at 5 eV CID collision energy.

CHAPTER VI

CONCLUSIONS AND FUTURE WORK

This research project was organized around two goals. The main effort was devoted to the development, characterization, and implementation of a new gas chromatographic/mass spectrometric (GC/MS) method of hydrocarbon type analysis (HTA) of jet fuels. The secondary effort was for the evaluation of ancillary techniques of mass spectrometry, such as alternative ionization and tandem mass spectrometry, for the determination of specific components or specific classes of components in jet fuels. A major advantage of these GC/MS techniques will be the ability to have a wide range of analyses available under one instrumental configuration. That is, a jet fuel sample may be analyzed by the hydrocarbon type method, and with minimal effort the instrumental configuration could be changed (for example to methane CI) in order to analyze the aromatic fraction in greater detail.

Summary of Results

Hydrocarbon Type Analysis

To most analytical chemists, the idea of type analysis is not very well known or understood. In this study much has been learned in regard to type analysis, specifically, hydrocarbon type analysis.

A new HTA method was developed for the analysis of jet fuels using GC/MS and the pre-existing ASTM inverse calibration matrix. The GC/MS/HTA method was characterized by several analytical techniques. The results of the GC/MS/HTA of fuels were compared to ASTM results. This did not provide much information since the accuracy of the ASTM results are not known.

The analysis of simple mixtures was conducted and compared to actual volume calculated results. These experiments were generally unsuccessful for the characterization of the GC/MS/HTA analysis due to the simplicity of the sample make-up which caused errors in the matrix calculation. However, results tend to support the "Teeter Rule" which basically states that no sample could be synthetically prepared which would be complex enough for the inverse calibration calculation to be valid.

A new method was applied for the characterization of this HTA analysis. In this method, jet fuel samples were perturbed by spiking the fuel with a known volume of a pure component or a mixture of a specific hydrocarbon type (such as Aromatic 150). This method maintained the required sample complexity for proper matrix calculation and allowed for an accurate assessment of the added spike. This method proved to be the most valuable technique for the characterization of the GC/MS/HTA method.

Calculation of Average Carbon Number

The most novel part of this research was the development of a new method for the determination of average carbon numbers. This method was based on GC/MS simulated distillation whereby the average carbon

number was determined based on the chromatographic separation. The average carbon number results were generally higher than the results calculated by the matrix method in the present GC/MS/HTA method or the ASTM method. We have more confidence in the simulated distillation methods, which suggest a serious limitation in the other two techniques. The GC/MS/HTA and ASTM methods both rely heavily on the average carbon number results, which therefore suggest a serious limitation in the volume percent results.

Ancillary Mass Spectrometric Methods

Summary of the studies of these ancillary MS techniques may well be considered suggestions for future work. No final methods were developed; rather suggestions were made for potential methods which could be developed.

Two alternative ionization techniques in mass spectrometry were evaluated for specific detectors of hydrocarbon types. Low energy electron ionization was demonstrated to be a specific detector for aromatics in the presence of aliphatic components. Methane chemical ionization, of common fuel components demonstrated very selective ion patterns for each specific hydrocarbon type. This method has good potential as a new hydrocarbon type analysis method, but would require extensive standardization.

Mass Spectrometry/mass spectrometry demonstrated great potential as a selective means of determining aromatics in the presence of paraffins as well as paraffins in the presence of aromatics. This was obtained using parent scan MS of selective daughter ions specific for each type. An actual jet fuel was analyzed using parent scan MS/MS. Good

agreement was obtained between the relative intensities of the mass chromatograms of each parent scan and the GC/MS/HTA results.

Differentiation between isomers of cycloparaffins and olefins was demonstrated using daughter scan MS/MS. These differences were dependent upon the collision energy, which demonstrates the potential use of energy-resolved collision-induced dissociation breakdown curve analysis. The ability to differentiate between these isomers is very important in regards to hydrocarbon type analysis, since large quantities of olefins may result in erroneous behavior of the GC/MS/HTA method.

The methods developed and the techniques evaluated represent a significant contribution to the analysis of jet fuels. Already, the GC/MS/HTA method has been implemented in the industrial sector. The method is simple and may be performed on most GC/MS instruments.

APPENDIX A

MATRIX INVERSION METHOD

Consider the matrices δ , θ , and Γ in which δ =the calibration mixture matrix, θ =the calibration data matrix of the Σ -ion series, and Γ =the inverse calibration matrix. The θ -calibration data matrix may be a square or unsymmetrical matrix, while the other matrices, δ and Γ are always square. The methods used for calculating both cases are shown below for the simplest examples, a 3x3 and a 3x4 θ -matrix. In both cases the θ -matrix equals the diagonal matrix shown below.

$$\theta = \begin{pmatrix} 100 & 0 & 0 \\ 0 & 100 & 0 \\ 0 & 0 & 100 \end{pmatrix}$$

For both cases, $\theta = \delta * \Gamma$ (the normalization function) enables the determination of the inverse calibration matrix, Γ since both δ and θ are known. The inverse calibration matrix is obtained by solving for Γ in the following way:

for the 3x3 δ -example;

$$\Gamma = \theta * \delta^{-1}$$

for the 3x4 δ -example;

$$\Gamma = (\delta^+ \delta)^{-1} \delta^T \theta.$$

The functions δ^+ , and δ^T are the complex conjugate and transpose of the matrix δ , respectively.

APPENDIX B

EXAMPLE GC/MS/HTA CALCULATION

The fuel used for the example calculation is 87-POSF-2532, a Jet-A type fuel. The results of the hydrocarbon type analysis for this fuel may be found in Chapter III.

The aromatic and paraffinic average carbon numbers for the example fuel were calculated to be 9.29 and 9.04, respectively. A weighted mixture of the carbon no. 9 and carbon no. 10 matrices must be used in calculating the volume percent of hydrocarbon type. The procedure involves calculating the volume percent twice; first based on carbon no. 9, then based on carbon no. 10. The final result is then determined by weighing the two results as determined by the actual aromatic and paraffinic average carbon numbers.

The example which follows will first illustrate the generic expressions for calculating the paraffin result for carbon no. 9. This is similar for calculations of all types and carbon numbers as is shown in the calculation of hydrocarbon type using the example fuel results and carbon no. 9 matrix. Finally the results hydrocarbon type analysis will be used for both Carbon No. 9 and 10 and the weighted result determined.

I. Generic Expression For Type Analysis

-

$$\begin{aligned} \text{C9 Paraffin} = & \text{C9}(1,1)(\Sigma 43\%) + \text{C9}(1,2)(\Sigma 41\%) + \text{C9}(1,3)(\Sigma 67\%) \\ & + \text{C9}(1,4)(\Sigma 77\%) + \text{C9}(1,5)(\Sigma 103\%) + \text{C9}(1,6)(\Sigma 128\%) \end{aligned}$$

Where C9(1,1) represents row one column one entry of the Carbon No. 9 inverse calibration matrix. The $\Sigma 43\%$ represents the percent contribution of $\Sigma 43$ to the ΣT ion count.

II. Sample calculation of the Carbon No. 9 results.

$$\begin{aligned} \text{C9 Paraffin} = & (.006043)(20.04) - (.000673)(35.79) + (.000071)(29.92) \\ & - (.000018)(9.79) - (.000095)(4.20) - (.000075)(0.26) \\ = & 0.9854\text{E-1} \end{aligned}$$

$$\begin{aligned} \text{C9 Monocycloparaffin} = & -(.001933)(20.04) + (.006183)(35.79) \\ & - (.001929)(29.92) - (.000130)(9.79) - (.000017)(4.20) + (.000011)(0.26) \\ = & 0.1235 \end{aligned}$$

$$\begin{aligned} \text{C9 Dicycloparaffin} = & (.000212)(20.04) - (.000822)(35.79) \\ & + (.006809)(29.92) + (.000003)(9.79) + (.000004)(4.20) - (.000006)(0.26) \\ = & 0.1786 \end{aligned}$$

$$\begin{aligned} \text{C9 Alkylbenzenes} = & (.000007)(20.04) - (.000040)(35.79) \\ & - (.000261)(29.92) + (.004015)(9.79) - (.000787)(4.20) - (.000248)(0.26) \\ = & 0.2684\text{E-1} \end{aligned}$$

$$\begin{aligned}
 \text{C9 Indanes/Tetralins} &= (.000001)(20.04) + (.000002)(35.79) \\
 &+ (.000020)(29.92) - (.000361)(9.79) + (.005496)(4.20) - (.000016)(0.26) \\
 &= 0.2023\text{E-1}
 \end{aligned}$$

$$\begin{aligned}
 \text{C9 Naphthalenes} &= -(.000090)(20.04) + (.000008)(35.79) + 0 + 0 \\
 &+ (.000001)(4.20) + (.005759)(0.26) \\
 &= -0.1574\text{E-4}
 \end{aligned}$$

The negative result for naphthalene is correct. This is a limitation of the matrix method since the volume percent value will ultimately be truncated to zero. Including the results for each type using carbon no. 10 matrix:

$$\begin{aligned}
 \text{C10 Paraffin} &= 0.7766\text{E-1} \\
 \text{C10 Monocycloparaffin} &= 0.1265 \\
 \text{C10 Dicycloparaffin} &= 0.1413 \\
 \text{C10 Alkylbenzene} &= 0.2756\text{E-1} \\
 \text{C10 Indanes/Tetralins} &= 0.2465\text{E-1} \\
 \text{C10 Naphthalenes} &= -0.8744\text{E-3}
 \end{aligned}$$

and application of the weighing expression:

$$\begin{aligned}
 \text{Weighted Type (paraffins)} &= \\
 &(\text{C9 Type}) + (\text{C9 Type} - \text{C10 Type})(\text{paraffin carbon number} - 9)
 \end{aligned}$$

Weighted Type (aromatic)=

(C9 Type) + (C9 Type - C10 Type)(aromatic carbon number - 9).

It should be pointed out again that the paraffin carbon number is used for the three saturated types and the aromatic for the three unsaturated types.

The example calculations are as follows:

$$\begin{aligned}\text{Paraffins} &= (0.9854\text{E-}1) + (0.7766\text{E-}1 - 0.9854\text{E-}1)(9.0355 - 9) \\ &= 0.9780\text{E-}1\end{aligned}$$

$$\begin{aligned}\text{Monocycloparaffins} &= (0.1235) + (0.1265 - 0.1235)(9.0355 - 9) \\ &= 0.1236\end{aligned}$$

$$\begin{aligned}\text{Dicycloparaffins} &= (0.1786) + (0.1413 - 0.1786)(9.0355 - 9) \\ &= 0.1773\end{aligned}$$

$$\begin{aligned}\text{Alkylbenzenes} &= (0.2684\text{E-}1) + (0.2756\text{E-}1 - 0.2684\text{E-}1)(9.2914 - 9) \\ &= 0.2705\text{E-}1\end{aligned}$$

$$\begin{aligned}\text{Indane/Tetralin} &= (0.2023\text{E-}1) + (0.2465\text{E-}1 - 0.2023\text{E-}1)(9.2914 - 9) \\ &= 0.2152\text{E-}1\end{aligned}$$

$$\begin{aligned}\text{Naphthalenes} &= -(0.1574\text{E-}4) - (0.8744\text{E-}3 + 0.1574\text{E-}4)(9.2914 - 9) \\ &= -0.2751\text{E-}3 = 0 \quad \text{since a negative volume percent is undefined.}\end{aligned}$$

$$\text{Total} = 0.4472$$

Note that the saturated components use the paraffin carbon number and the unsaturated components use the aromatic carbon number. A negative result is truncated to zero. The values are now normalized to 100% and represent the final volume percent of each hydrocarbon type.

The results are:

$$\text{Paraffins} = (0.9780\text{E-}1/0.4472)*100 = 21.87$$

$$\text{Monocycloparaffins} = (0.1236/0.4472)*100 = 27.64$$

$$\text{Dicycloparaffins} = (0.1773/0.4472)*100 = 39.64$$

$$\text{Alkylbenzenes} = (0.2705\text{E-}1/0.4472)*100 = 6.05$$

$$\text{Indane/Tetralin} = (0.2705\text{E-}1/0.4472)*100 = 4.81$$

$$\text{Naphthalenes} = (0/0.4472)*100 = 0.00$$

APPENDIX C

GC/MS/HTA TURBO BASIC PROGRAM

Turbo Basic Program
GCMSHTA.BAS

September 15, 1987

This program was written to perform the calculations set out in the GC/MS Hydrocarbon Type Analysis Method for Jet Fuels developed by Michael J. Gehron and Richard A. Yost at the University of Florida, Department of Chemistry. Funding and support was provided by Wright-Patterson Air Force Base-Fuels Division contract no. F33615-85-C-2508, through United Technologies-Pratt & Whitney.

GC/MS HYDROCARBON TYPE ANALYSIS PROGRAM

MAJOR VARIABLES

C78, C91, etc	ION INTENSITIES FROM GC/MS
ISUM(N)	ION SUMMATION VALUES FOR EACH HYDROCARBON TYPE CALCULATED FROM THE GC/MS MASS CHROMATOGRAMS
AACN	AROMATIC AVERAGE CARBON NUMBER
PACN	PARAFFIN AVERAGE CARBON NUMBER
C6(J,I) - C10(J,I)	VARIABLE ARRAYS FOR INVERSE CALIBRATION MATRIX DATA STORAGE

=====

READING IN OF ION INTENSITY DATA

CLS

```

PRINT "ENTER DATA INPUT SOURCE-----KEYBOARD(K) OR DISK(D)
DIM ISUM(6)
INPUT A$
IF A$="D" OR A$="d" GOTO 10
INPUT "ENTER DATA FILE NAME TO CREATE
(DRIVE:\PATH\FILENAME.DAT)";B$
OPEN "O",1,B$
PRINT "ENTER AROMATIC ION INTENSITIES 78,91,92,105,106,
      119,120,133,134"
PRINT "147,148,161,162"
PRINT " "
INPUT C78,C91,C92,C105,C106,C119,C120,C133,C134,C147,C148,C161,C162

PRINT "ENTER PARAFFINIC ION INTENSITIES 84,85,86,98,99,100,
      112,113,114"
PRINT "126,127,128,140,141,142,154,155,156,168,169,170"
INPUT C84,C85,C86,C98,C99,C100,C112,C113,C114,C126,C127,C128
INPUT C140,C141,C142,C154,C155,C156,C168,C169,C170
PRINT #1,C78,C91,C92,C105,C106,C119,C120,C133,C134,
      C147,C148,C161,C162
PRINT #1,C84,C85,C86,C98,C99,C100,C112,C113,C114,C126,C127,C128
PRINT #1,C140,C141,C142,C154,C155,C156,C168,C169,C170

PRINT "ENTER ION SUMMATION VALUES FOR EACH HYDROCARBON TYPE"
FOR N=1 TO 6
INPUT ISUM(N)
PRINT #1,ISUM(N)
NEXT N
CLOSE #1
GOTO 40

10 PRINT "ENTER DATA FILE NAME (DRIVE:\PATH\FILENAME.DAT)"
PRINT " "
INPUT B$
OPEN "I",2,B$
INPUT #2,C78,C91,C92,C105,C106,C119,C120,
      C133,C134,C147,C148,C161,C162
INPUT #2,C84,C85,C86,C98,C99,C100,C112,C113,C114,C126,C127,C128
INPUT #2,C140,C141,C142,C154,C155,C156,C168,C169,C170

DECIDE IF ION SUMMATION VALUES WILL BE ENTERED WITH KEYBOARD OR
FILE

INPUT "IS THERE A HTA ION SUMMATION FILE ???? (Y)ES OR (N)O"; C$
IF C$="Y" OR C$="y" GOTO 15
CLOSE #2
PRINT "ENTER ION SUMMATION VALUES FOR EACH HYDROCARBON TYPE"
OPEN "A",2,B$
FOR N=1 TO 6
INPUT ISUM(N)
PRINT #2,ISUM(N)
NEXT N

```

```
CLOSE #2
GOTO 40
```

```
15  FOR N=1 TO 6
      INPUT #2, ISUM(N)
NEXT N
30  CLOSE #2
```

CALCULATION OF AROMATIC AVERAGE CARBON NUMBER

CALCULATION OF MONOISOTOPIC PEAKS

```
40  M92=C92-(.0769*C91)
    M106=C106-(.0880*C105)
    M120=C120-(.0991*C119)
    M134=C134-(.1102*C133)
    M148=C148-(.1212*C147)
    M162=C162-(.1323*C161)
```

CONVERT MONOISOTOPIC PEAKS TO MOLAR BASIS

```
MB78=C78*1.0
IF MB78<0 THEN MB78=0
MB92=M92*1.7
IF MB92<0 THEN MB92=0
MB106=M106*2.2
IF MB106<0 THEN MB106=0
MB120=M120*2.4
IF MB120<0 THEN MB120=0
MB134=M134*2.7
IF MB134<0 THEN MB134=0
MB148=M148*2.8
IF MB148<0 THEN MB148=0
MB162=M162*2.9
IF MB162<0 THEN MB162=0
MBTOT=MB78+MB92+MB106+MB120+MB134+MB148+MB162
```

NORMALIZE MOLAR BASIS AND CONVERT TO RELATIVE MOLE FRACTION

```
MF78=MB78/MBTOT*6
MF92=MB92/MBTOT*7
MF106=MB106/MBTOT*8
MF120=MB120/MBTOT*9
MF134=MB134/MBTOT*10
MF148=MB148/MBTOT*11
MF162=MB162/MBTOT*12
```

AROMATIC AVERAGE CARBON NUMBER

```
AACN=MF78+MF92+MF106+MF120+MF134+MF148+MF162
PRINT "AROMATIC AVERAGE CARBON NUMBER EQUALS",AACN
```

CALCULATION OF PARAFFIN AVERAGE CARBON NUMBER

CALCULATION OF MONOISOTOPIC PEAKS

```

M86=C86-(.0668*C85)+(.0026*C84)-(.014*M92)-(.008*M106)-(.008*M120)
M100=C100-(.0779*C99)+(.0034*C98)
M114=C114-(.0890*C113)+(.0044*C112)
M128=C128-(.1001*C127)+(.0055*C126)
M142=C142-(.1130*C141)+(.0068*C140)
M156=C156-(.1224*C155)+(.0081*C154)
M170=C170-(.1335*C169)+(.0096*C168)

```

CONVERT MONOISOTOPIC PEAKS TO MOLAR BASIS

```

MB86=M86*1.0
IF MB86<0 THEN MB86=0
MB100=M100*.92
IF MB100<0 THEN MB100=0
MB114=M114*1.4
IF MB114<0 THEN MB114=0
MB128=M128*1.8
IF MB128<0 THEN MB128=0
MB142=M142*1.9
IF MB142<0 THEN MB142=0
MB156=M156*2.0
IF MB156<0 THEN MB156=0
MB170=M170*2.1
IF MB170<0 THEN MB170=0
MBTOL=MB86+MB100+MB114+MB128+MB142+MB156+MB170

```

NORMALIZE MOLAR BASIS AND CONVERT TO RELATIVE MOLE FRACTION

```

MF86=MB86/MBTOL*6
MF100=MB100/MBTOL*7
MF114=MB114/MBTOL*8
MF128=MB128/MBTOL*9
MF142=MB142/MBTOL*10
MF156=MB156/MBTOL*11
MF170=MB170/MBTOL*12

```

PARAFFINIC AVERAGE CARBON NUMBER

```

PACN=MF86+MF100+MF114+MF128+MF142+MF156+MF170
PRINT "PARAFFIN AVERAGE CARBON NUMBER",PACN

```

CALCULATION OF VOLUME % OF HYDROCARBON TYPES

DIMENSIONING OF VARIABLE ARRAYS

```

DIM C6(6,6),C7(6,6),C8(6,6),C9(6,6),C10(6,6),V(6),M6(4),M7(5)
DIM M8(6),M9(6),M10(6)

```

READING OF CALIBRATION MATRIX DATA FOR C6

```

FOR J=1 TO 4
  FOR I=1 TO 4

```

```

      READ C6(J,I)
    NEXT I
  NEXT J
  DATA .009016,-.001368,.000257,-.000003,-.004471,.010285,-.002391
  DATA -.000002,.000100,-.000258,.004325,0,.000017,-.000048,-.000149,

  DATA .005117

```

READING OF CALIBRATION MATRIX DATA FOR C7

```

  FOR J=1 TO 5
    FOR I=1 TO 5
      READ C7(J,I)
    NEXT I
  NEXT J
  DATA .007241,-.000655,.000105,-.000100,-.000100,-.002542,.007283,
  DATA -.001695,-.000051,-.000035,.000167,-.000523,.004387,.000001
  DATA,.000003,.000010,-.000044,-.000134,.004576,-.000897,0,0
  DATA -.000002,0,.005424

```

READING OF CALIBRATION MATRIX DATA FOR C8

```

  FOR J=1 TO 6
    FOR I=1 TO 6
      READ C8(J,I)
    NEXT I
  NEXT J
  DATA .006449,-.000584,.000090,-.000011,-.000105,-.000082,-.001902
  DATA .006132,-.001428,-.000063,-.000029,.000006,.000128,-.000469
  DATA .004375,.000001,.000003,-.000004
  DATA .000007,-.000049,-.000125,.004375,-.000857,-.000271,0,.000002
  DATA .000004,-.000207,.005465,-.000026,0,0,0,0,0,.005757

```

READING OF CALIBRATION MATRIX DATA FOR C9

```

  FOR J=1 TO 6
    FOR I=1 TO 6
      READ C9(J,I)
    NEXT I
  NEXT J
  DATA .006043,-.000673,.000071,-.000018,-.000095,-.000075,-.001933
  DATA .006183,-.001929,-.000130,-.000017,.000011,.000212,-.000822
  DATA .006809,.000003,.000004,-.000006
  DATA .000007,-.000040,-.000261,.004015,-.000787,-.000248,.000001
  DATA .000002,.000020,-.000361,.005496,-.000016,-.000090,.000008
  DATA 0,0,.000001,.005759

```

READING OF CALIBRATION MATRIX DATA FOR C10

```

  FOR J=1 TO 6
    FOR I=1 TO 6
      READ C10(J,I)
    NEXT I
  NEXT J
  DATA .005766,-.001562,.000606,.000001,
  DATA -.000025,-.000070,-.001897,.007443

```

```

DATA -.003315,-.000270,-.000004,.000015,.000666,
      -.002792,.007592,.000087
DATA -.000032,-.000009
DATA -.000006,.000021,-.000201,.003903,
      -.001240,-.000238,.000002,-.000001
DATA .000029,-.000709,.007315,-.000007,
      -.000120,.000033,-.000012,-.000006
DATA -.000174,.005761

```

```

DETERMINATION OF CARBON NUMBER MATRIX TO BE USED FOR ALKYL BENZENES
AND CALCULATION OF VOLUME PERCENT OF AROMATIC TYPES
IF AACN>=6 AND AACN<=10 GOTO 100
PRINT "AROMATIC CARBON NUMBER";AACN;"IS OUTSIDE RANGE OF MATRIX"
IF AACN<6 THEN AACN=6
IF AACN>10 THEN AACN=10
100 FOR I=6 TO 10
      IF AACN<I THEN GOTO 200
      NEXT I
200 AM1=I
      AM2=I-1
      SEND=AM2
300 IF SEND=6 THEN GOSUB 1000
      IF SEND=7 THEN GOSUB 1100
      IF SEND=8 THEN GOSUB 1200
      IF SEND=9 THEN GOSUB 1300
      IF SEND=10 THEN GOSUB 1400
      IF SEND=AM1 THEN GOTO 400
      X4=V(4)
      X5=V(5)
      X6=V(6)
      SEND=AM1
      GOTO 300
400 Y4=V(4)
      Y5=V(5)
      Y6=V(6)
      R=1
      IF AM2<AM1 THEN R=(AACN-AM2)/(AM1-AM2)
      Z4=R*(Y4-X4)+X4
      Z5=R*(Y5-X5)+X5
      Z6=R*(Y6-X6)+X6

```

```

DETERMINATION OF CARBON NUMBER MATRIX TO BE USED FOR PARAFFINS
AND CALCULATION OF VOLUME PERCENT OF PARAFFINIC TYPES
IF PACN>=6 AND PACN<=10 GOTO 500
PRINT "PARAFFIN CARBON NUMBER";PACN;"IS OUTSIDE RANGE OF MATRIX"
IF PACN<6 THEN PACN=6
IF PACN>10 THEN PACN=10
500 FOR I=6 TO 10
      IF PACN<I THEN GOTO 600
      NEXT I

```

```

600 PM1=I
    PM2=I-1
    SEND=PM2
700 IF SEND=6 THEN GOSUB 1000
    IF SEND=7 THEN GOSUB 1100
    IF SEND=8 THEN GOSUB 1200
    IF SEND=9 THEN GOSUB 1300
    IF SEND=10 THEN GOSUB 1400
    IF SEND=PM1 THEN GOTO 800
    X1=V(1)
    X2=V(2)
    X3=V(3)
    SEND=PM1
    GOTO 700
800 Y1=V(1)
    Y2=V(2)
    Y3=V(3)
    R=1
    IF PM2<PM1 THEN R=(PACN-PM2)/(PM1-PM2)
    Z1=R*(Y1-X1)+X1
    Z2=R*(Y2-X2)+X2
    Z3=R*(Y3-X3)+X3

```

VOLUME FRACTION RESULTS AT LEAST ZERO PERCENT

```

IF Z1<0 THEN Z1=0
IF Z2<0 THEN Z2=0
IF Z3<0 THEN Z3=0
IF Z4<0 THEN Z4=0
IF Z5<0 THEN Z5=0
IF Z6<0 THEN Z6=0

```

NORMALIZATION OF RESULTS TO 100%

```

Z=Z1+Z2+Z3+Z4+Z5+Z6
Z1=Z1/Z*100
Z2=Z2/Z*100
Z3=Z3/Z*100
Z4=Z4/Z*100
Z5=Z5/Z*100
Z6=Z6/Z*100

```

PRINTING OF RESULTS

INPUT DATA-----

```

LPRINT "HYDROCARBON TYPE ANALYSIS ON      ";B$
LPRINT " "
LPRINT " "
LPRINT "AROMATIC ION INTESITIES ENTERED FOR CARBON NUMBER
      CALCULATION"

```

```

LPRINT " "
LPRINT " C78          C91          C92          C105
          C106"
LPRINT C78,C91,C92,C105,C106
LPRINT " "
LPRINT " C119          C120          C133          C134"
LPRINT C119,C120,C133,C134
LPRINT " "
LPRINT " C147          C148          C161          C162
LPRINT C147,C148,C161,C162
LPRINT " "
LPRINT "PARAFFIN ION INTENSITIES ENTERED FOR CARBON NUMBER
      CALCULATION"
LPRINT " "
LPRINT " C84          C85          C86          C98
          C99"
LPRINT C84,C85,C86,C98,C99
LPRINT " "
LPRINT " C100          C112          C113          C114
          C126"
LPRINT C100,C112,C113,C114,C126
LPRINT " "
LPRINT " C127          C128          C140          C141
          C142"
LPRINT C127,C128,C140,C141,C142
LPRINT " "
LPRINT " C154          C155          C156          C168
          C169"
LPRINT C154,C155,C156,C168,C169
LPRINT " "
LPRINT " C170"
LPRINT C170
LPRINT " "
LPRINT "ION SUMMATION VALUES ENTERED FOR VOLUME PERCENT
      CALCULATION"
LPRINT " "
LPRINT USING "PARAFFINS          ###.##";ISUM(1)
LPRINT USING "MONOCYCLOPARAFFINS  ###.##";ISUM(2)
LPRINT USING "DICYCLOPARAFFINS    ###.##";ISUM(3)
LPRINT USING "ALKYLBENZENES       ###.##";ISUM(4)
LPRINT USING "INDANES/TETRALINS    ###.##";ISUM(5)
LPRINT USING "NAPHTHALENES        ###.##";ISUM(6)
LPRINT " "
LPRINT " "

OUTPUT DATA (RESULTS)-----

      LPRINT "HYDROCARBON TYPE ANALYSIS RESULTS--"
      LPRINT "-----"
      LPRINT " "
      LPRINT USING "AROMATIC AVERAGE CARBON NUMBER    ###.####";AACN
      LPRINT " "

```

```
LPRINT USING "PARAFFINIC AVERAGE CARBON NUMBER   ###.###" ; PACN
LPRINT " "
```

```
LPRINT "VOLUME PERCENT OF HYDROCARBON TYPES"
```

```
LPRINT " "
```

```
LPRINT USING "PARAFFINS           ###.###"; Z1
LPRINT USING "MONOCYCLOPARAFFINS  ###.###"; Z2
LPRINT USING "DICYCLOPARAFFINS    ###.###"; Z3
LPRINT USING "AROMATICS           ###.###"; Z4
LPRINT USING "INDANES/TETRALINS   ###.###"; Z5
LPRINT USING "NAPHTHALENES        ###.###"; Z6
LPRINT CHR$(12)
```

```
STOP
```

MATRIX CALCULATION SUBROUTINES

C6 SUBROUTINE

```
1000   FOR J=1 TO 4
        FOR I=1 TO 4
            M6(I)=ISUM(I)*C6(J,I)
        NEXT I
        FOR K=1 TO 4
            SUM6=SUM6+M6(K)
        NEXT K
        V(J)=SUM6
        SUM6=0
    NEXT J
    V(5)=0
    V(6)=0
    RETURN
```

C7 SUBROUTINE

```
1100   FOR J=1 TO 5
        FOR I=1 TO 5
            M7(I)=ISUM(I)*C7(J,I)
        NEXT I
        FOR K=1 TO 5
            SUM7=SUM7+M7(K)
        NEXT K
        V(J)=SUM7
        SUM7=0
    NEXT J
    V(6)=0
    RETURN
```

C8 SUBROUTINE

```
1200   FOR J=1 TO 6
        FOR I=1 TO 6
            M8(I)=ISUM(I)*C8(J,I)
        NEXT I
        FOR K=1 TO 6
            SUM8=SUM8+M8(K)
```

```
      NEXT K  
      V(J)=SUM8  
      SUM8=0  
NEXT J  
RETURN
```

```
      C9 SUBROUTINE  
1300   FOR J=1 TO 6  
        FOR I=1 TO 6  
          M9(I)=ISUM(I)*C9(J,I)  
        NEXT I  
        FOR K=1 TO 6  
          SUM9=SUM9+M9(K)  
        NEXT K  
        V(J)=SUM9  
        SUM9=0  
NEXT J  
RETURN
```

```
      C10 SUBROUTINE  
1400   FOR J=1 TO 6  
        FOR I=1 TO 6  
          M10(I)=ISUM(I)*C10(J,I)  
        NEXT I  
        FOR K=1 TO 6  
          SUM10=SUM10+M10(K)  
        NEXT K  
        V(J)=SUM10  
        SUM10=0  
NEXT J  
RETURN
```

APPENDIX D

PRELIMINARY TEST METHOD FOR HYDROCARBON TYPE ANALYSIS OF JET FUEL BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

This is a preliminary standard test method developed By Michael J. Gehron and Richard A. Yost at the University of Florida Chemistry Department. The format of the ASTM Standard D-2789-81 was used in preparation of this document. Funding and support was provided by Wright-Patterson Air Force Base-Fuels Division contract no. F33615-85-C-2508, through United Technologies-Pratt & Whitney. Special acknowledgements are extended to Bill Edwards of Pratt & Whitney for his guidance in the fuels area and also to Sue Guisinger, also of Pratt & Whitney, for her contribution to the BASIC program for hydrocarbon type analysis.

1. Scope

1.1 This method covers the determination by Gas Chromatography/Mass Spectrometry of the total paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes, indanes and tetralins, and naphthalenes in jet fuels with an average carbon number of the saturated and unsaturated fractions between six and ten.

2. Applicable Documents

2.1 ASTM Standards

D 2789 Test Method for Hydrocarbon Types in Low Olefinic Gasoline
by Mass Spectrometry

D 86 Method for Distillation of Petroleum Products

D 875 Method for Calculation of Olefin and Aromatics in Petroleum
Distillates from Bromine Number and Acid Absorption

D 1319 Test Method for Hydrocarbon Types in Liquid Petroleum
Products by Fluorescent Indicator

D 2001 Test Method for Depentanization of Gasoline and Naphthas

D 2002 Method for Isolation of Representative Saturates Fraction
from Low-Olefinic Petroleum Naphthas

2.2 Other Documents

Brown, R.A. Anal. Chem. 1951, 23, 430.

3. Summary of Method

Samples are analyzed by GC/MS using the classical ASTM 2789 inverse calibration matrices (section 2.1). The neat jet fuel samples are introduced into the mass spectrometer with a short bonded phase capillary column and split mode injection.

Data is collected using mass summation chromatography of the characteristic mass fragments of each hydrocarbon type (see section 5). Data is also collected for the individual mass fragments used in the calculation of average carbon number (see section 11). These results are subjected to a BASIC computer program which calculates the average carbon numbers of the combined saturated and combined unsaturated

fractions, and the volume percent of each hydrocarbon type.

4. Significance and Use

It is desired to have a hydrocarbon type analysis which may be applied the boiling point range of modern jet fuels and be amenable to modern mass spectrometric instrumentation. Hydrocarbon type analysis (HTA) of jet fuel is important for the design, operation, and maintenance of jet engines.

5. Definitions

5.1 Summation ions of characteristic hydrocarbon types

5.1.1 $\Sigma 43$ (paraffins)=total intensity of (m/z) 43+57+71+99.

5.1.2 $\Sigma 41$ (monocycloparaffins)=total intensity of (m/z)
41+55+69+83+97.

5.1.3 $\Sigma 67$ (dicycloparaffins)=total intensity of (m/z)
67+68+81+82+95+96.

5.1.4 $\Sigma 77$ (alkylbenzenes)=total intensity of (m/z) 77+78+79+91+92+
105+106+119+120+133+134+147+148+161+162.

5.1.5 $\Sigma 103$ (indans/tetralins)=total ion intensity of (m/z) 103+104
117+118+131+132+145+146+159+160.

5.1.6 $\Sigma 128$ (naphthalenes)=total ion intensity of (m/z)
128+141+142+155.

5.1.7 ΣT =Total ion summation of $\Sigma 43+\Sigma 41+\Sigma 67+\Sigma 77+\Sigma 103+\Sigma 128$.

5.2 Mass summation chromatogram is the mass chromatogram of each ion summation value (Σ values) for example, the mass summation chromatogram of the $\Sigma 43$ ion series is the mass chromatogram of the combined (summed) $\Sigma 43$ ion series as shown in section 5.1.1 above.

6. Apparatus

6.1 Mass Spectrometry

The mass spectrometer used is a Finnigan TSQ 45 operated in the single stage quadrupole mode. Any single stage quadrupole mass spectrometer capable of interfacing to a capillary gas chromatograph may be used. The ionization source is operated in the electron ionization (EI) mode; filament current, 300 μ A; electron energy, 70 eV; source temperature, 190°C. The mass spectrometer is scanned from 35 to 650 amu in 0.95 sec with a rest time of 0.05 sec.

6.2 Sample Introduction

The sample fuel is injected onto a 3 meter capillary column which is inserted directly into the ion source of the mass spectrometer. Split type injections of 0.1 to 0.5 μ L are made with a ratio of 50:1. Care must be taken in developing a reproducible injection technique. The syringe must be thoroughly rinsed with hexane or another suitable solvent to remove the previous fuel sample left over in the syringe barrel. The syringe must then be thoroughly rinsed with the fuel sample to be injected in order to insure removal of any remaining hexane. Alternatively a 1 μ L hexane plug may be maintained in the syringe volume. This eliminates syringe sample memory and aids in reproducible injections. The hexane peak, however, must be resolved from the components of the sample fuel. For fuels which contain components in the hexane eluting range, a longer column and/or sub-ambient column temperatures may also be considered as methods of

resolving the fuel components. If the fuel contains hexane or any co-eluting component, neat sample injection is required.

6.3 Chromatography

The capillary column used is a J&W Durabond DB5, 3 m long x 0.25 mm i.d. x 1.0 μ m film thickness nonpolar column. The column carrier gas is helium, column temperature, 40°C for 0.5 min, then programmed to 280°C at 15°C/min. A longer column may be substituted if desired, but increased analysis times will result.

7. Reference Samples

Synthetic JP-8X or another synthetic mixture or a jet fuel of known composition is used for the performance test.

8. Performance Test

Calibrate (mass assignment) the instrument according to its own specifications. Tune the instrument to obtain the proper relative ion abundances for the calibration compound used. Maintain a constant ion ratio for two or more sets of characteristic ions of the calibration compound. In this laboratory, the Finnigan MAT Model TSQ 45 uses perfluorotri-n-butylamine as the calibration compound. An ion intensity ratio between 1.2 and 1.8 is maintained for m/z 69 : m/z 219 and between 1.5 and 2.0 for m/z 502 : m/z 220. These ion ratios cover the total mass range of interest. Reproducible tuning of the mass range is critical in maintaining day to day accuracy.

Perform a HTA on the reference standard mixture (section 10). The

results should agree to known concentrations to within the same limits specified in ASTM D-2789 as shown in Table I.

Table I
Performance Test Limits of Error

<u>Hydrocarbon Type</u>	<u>Percent</u>
Total Paraffins	± 0.8
Total Cycloparaffins	± 1.3
Total Aromatics	± 0.7

9. Sample Preparation

9.1 Depentanize the sample in accordance to Method D2001.

9.2 Determine the olefin content of the depentanized sample in accordance with Method D1319 or D 875.

9.3 Alternate GC/MS/MS method for the determination of olefin content is currently being developed in this laboratory.

9.4 Store the working sample in a septum vial in which the septum is easily puncturable by a standard gas chromatographic syringe and which can be easily replaced by a new septum for storage.

10. Procedure

10.1 Tune the Mass Spectrometer as described in Section 6.1.

10.2 Run the performance test and compare results to Table I.

Replicate analyses of the performance standard may be performed to obtain daily precision values. Any jet fuel sample within the scope of the analysis may serve as a precision check sample. If the accuracy of the performance test is not inadequate, one should consider the state of the reference standard, the tuning of the mass spectrometer or the ability of the analyst. If the precision of the analysis is inadequate, one should consider the sample injection technique, the instrumental noise of the mass spectrometer, or the ability of the analyst.

10.3 Injection Technique- Using a 5 μL syringe (a 10 μL syringe may be substituted) obtain 1 to 1.5 μL of fuel. Pull back on the syringe plunger, removing the fuel from the needle, and record the sample volume. Pierce the injection port septum with the syringe needle and count to three, allowing the entire injection needle to equilibrate to the injection port temperature and minimizing component discrimination. Inject the sample at a rate of 1 μL per second and hold for another three count. Remove the syringe and record the volume. The difference will indicate the exact volume injected.

10.4 Instrumentation- The gas chromatographic conditions should be set as described in section 6.3. The mass spectrometer conditions should be set as described in section 6.1.

10.5 Data Analysis- Obtain the ion intensities which are used for carbon number calculations (section 11), as well as the relative percentage of each hydrocarbon type from the mass summation chromatograms (section 11). Input these values into the accompanying BASIC program (see Appendix B).

11. Calculations

11.1 Average Carbon Number- The method of calculation of aromatic and paraffinic carbon number is covered in the ASTM 2789 standard (section 11.2) and will not be reproduced here. The values are calculated using the BASIC program.

11.2 Calculation of Hydrocarbon Type- The method of calculation of hydrocarbon type is covered somewhat briefly in the ASTM 2789 standard (section 11.3). A sample calculation and result is given in the appendix. The BASIC program calculates the volume percent of each hydrocarbon type.

11.3 Olefinic Content- At present the monocycloparaffin result represents the contribution of monocycloparaffin and olefin content. If the olefinic content is determined by additional means and the content is less than 3%, subtract this amount from the monocycloparaffin results.

12. Calibration

Calibration is obtained in accordance to the ASTM 2789 standard inverse calibration matrices (section 12 and Table I of the standard). The inverse calibration matrices are incorporated into the BASIC program which calculates volume percent of hydrocarbon types.

13. Precision and Accuracy

13.1 Precision- There has been no interlaboratory precision test of the method. Day to day precision of the method for several test

fuels are shown in the appendix results section.

13.2 Accuracy- The results of several test fuels are compared to actual ASTM 2789 results. It should be noted however, that ASTM 2789 results may not necessarily represent the actual hydrocarbon type make-up. Examination of recipe fuels (pseudo fuels with known make-up) may indicate accuracy, but there is some controversy as to the validity of such relatively simple pseudo-fuels for the matrix calculation method.

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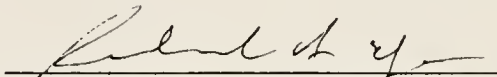
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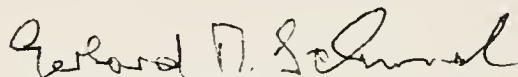
BIOGRAPHICAL SKETCH

Michael Joe Gehron was born in Fort Lauderdale, Florida, on June 27, 1956 as a third generation Fort Lauderdale native. He attended Nova High School in Fort Lauderdale, Florida, and graduated in May, 1974. He then attended Broward Community College and graduated with an A.A. degree on June, 1977. He then attended Florida State University and received his B.S. degree in chemistry in December, 1979. Mike then worked with David C. White, an environmental microbiologist-chemist, for the next four years as a chemist. He came to the University of Florida in July, 1983, and received a Master of Science in electroanalytical chemistry in May, 1985. He continued on with Rick Yost at the university and is receiving his Ph.D. in analytical chemistry. Mike is the proud father of Laura Ann Gehron and his soon to be second child. Mike will continue his work in GC/MS and analytical methods at the materials laboratory of Pratt and Whitney in West Palm Beach, Florida.

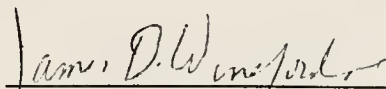
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Richard A. Yost, Chairman
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Associate Professor of Chemistry

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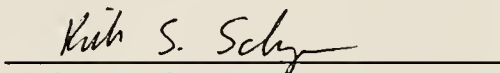

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

April, 1988

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